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JACA Corp., Fort Washington, PA

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The Tenth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste was held April 3 through 5, 1984. This volume is a compilation of speakers' papers and poster presenters' abstracts for Session B, Hazardous Waste Incineration and Treatment. Subjects include innovative technology, lab-scale research projects, pilot and full-scale incineration projects, combustion of hazardous waste in boilers and in industrial processes, and hazardous waste treatment and cost studies.

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Proceedings of the Tenth Annual Research Symposium
at Ft. Mitchell, Kentucky, April 3-5, 1984

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

We at the Industrial Environmental Research Laboratory in Cincinnati have always believed that an important part of our responsibility is to provide to the technical community the results of our various projects in as timely a manner as possible. This Proceedings document, containing papers presented at our 1984 Research Symposium, presents project summaries and interim results of our current work for this purpose, since much of the work discussed may not be available in final reports for some time. We hope that you will find these papers useful. Any questions or comments that you might have should be directed to the Chief, Incineration Research Group, IERL.

David G. Stephan
Director
Industrial Environmental
Research Laboratory

PREFACE

These Proceedings are intended to disseminate up-to-date information on extramural research projects concerning land disposal, incineration, and treatment of hazardous waste. These projects are funded by the U.S. Environmental Protection Agency's Office of Research and Development and have been reviewed in accordance with the requirements of EPA's Peer and Administrative Review Control System.

ABSTRACT

The Tenth Annual Research Symposium on Land Disposal, Remedial Action, Incineration and Treatment of Hazardous Waste was held in Fort Mitchell, Kentucky, April 3 through 5, 1984. The purpose of the symposium was to present to persons concerned with hazardous waste management the latest significant findings of ongoing and recently completed research projects funded by the Industrial Environmental Research Laboratory's Energy Pollution Control Division and the Municipal Environmental Research Laboratory's Solid and Hazardous Waste Research Division.

This volume is a compilation of speakers' papers and poster presenters' abstracts for Session B, Hazardous Waste Incineration and Treatment. Subjects include innovative technology, lab-scale research projects, pilot and full-scale incineration projects, combustion of hazardous waste in boilers and in industrial processes, and hazardous waste treatment and cost studies.

This document covers hazardous waste incineration and treatment only. A separate document for Session A, Hazardous Waste Land Disposal, is available from the Municipal Environmental Research Laboratory.

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ENVIRONMENTAL CHARACTERIZATION OF THE COMBUSTION OF WASTE OIL IN SMALL COMMERCIAL BOILERS

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ABSTRACT

Tests were conducted on seven boilers in the size range of 0.4 to 20 X 10^6 British thermal units per hour (Btu/hr) which were burning a waste oil fuel spiked with a series of organic chemical compounds commonly found in waste oil. Compounds tested included chlorinated solvents such as chloroform, trichloroethylene, trichloroethane, tetrachloroethylene and several chlorinated benzenes. Test results are presented here in terms of stack gas emission concentrations and destruction efficiencies for the various compounds.

INTRODUCTION AND PURPOSE OF THE PROJECT

In recent years the environmental impact of the disposal of used oils has been an area of growing concern. Numerous studies conducted by state and Federal agencies have documented the presence of contaminants such as polynuclear aromatics (PNAs), chlorinated hydrocarbons and heavy metals in samples of used motor oils. One of the more common and widespread practices for disposing of used oils is burning as a supplemental fuel. In some cases, waste oil is burned directly; in others, it is blended with other fuel feedstocks.

The disposal of waste materials in boilers is of particular interest because to date, there has been little documentation of the extent to which chemical contaminants in waste oil are destroyed during the combustion process.

In this project, tests were conducted on boilers in the size range of 0.4 to 20 X 10^6 Btu/hr. These are commonly classified as commercial sources, as opposed to industrial or electric utility sources. Commercial boilers are of particular interest with regard to waste oil disposal for several reasons. These units generally would use untreated or poorly characterized waste fuels. They could be expected to provide less efficient combustion because of the generally intermittent mode of operation. In addition, their widespread distribution and their low stack heights make their emissions more proximate to the general population.

APPROACH

Seven boilers were designated for testing in the program. The units were selected so as to provide a representative cross section of the commercial boiler population. A 4000 gallon lot of used automotive oil was obtained in order to maintain a consistent supply of waste fuel for the program. Portions of the base stock oil were spiked with predetermined amounts of selected organic compounds which are typically found in waste oil and in some cases are considered hazardous waste materials. The selected compounds were as follows:

- chloroform
- 1,1,1-trichloroethane
- trichloroethylene
- tetrachloroethylene
- trichlorobenzene
- dichloronaphthalene
- 2,4,5-trichlorophenol
- chlorotoluene

These compounds were chosen to simulate a typical waste oil, based on data from a cross section of representative waste oils.[1]

Measurements were conducted at each of the sites to determine the atmospheric emissions of particulate, inorganic compounds (principally lead and hydrogen chloride (HCl), and volatile organic and semivolatile organic material. The destruction and removal efficiencies (DRE) for each of the spiked components were also determined.

TEST RESULTS

Destruction and Removal Efficiencies

The flue gas emissions of the organic compounds of interest correspond to destruction and removal efficiencies of 99.4 to 99.99 percent as indicated in Table 1. There were no strong correlations between destruction efficiency and boiler size or firing technique. One trend that is apparent from the data is that the destruction efficiencies for the semivolatile compounds are consistently higher than those of the volatile compounds. The fact that generally higher DRE's were achieved for the semivolatile components, trichlorobenzene, dichloronaphthalene and trichlorophenol, is consistent with the ranking of the spike compounds on the EPA Hierarchy of Waste Incinerability.[2]

Generally the lowest DRE's were found in site A, the only boiler rated at less than 1 X 10^6 Btu/hr. This unit normally fires a No. 2 fuel oil and its adaption to firing waste oil proved difficult. Eventually dilution of the waste oil on a 1:1 basis with No. 2 oil was required for acceptable operation. Even with this modification, the combustion efficiency and destruction efficiencies were significantly lower than the other units.

Concentrations of Contaminants in Combustion Gases

In Table 2 are shown the concentration ranges in the stack gas of the compounds studies within the program. In general, concentrations ranged from 40 to 400 micrograms per cubic meter ($\mu g/m^3$) for the volatile compounds and from about 10 to 50 $\mu g/m^3$ for the semivolatile compounds. On a volume/volume (v/v) basis, these are very low concentrations. As an example, a range of 40 to 400 $\mu g/m^3$ for a compound such as trichloroethylene corresponds to a concentration of 7.4 to 74 parts per billion (ppb) on a v/v basis. Conducting emission tests at these low concentrations required extensive refinement of available emission source testing techniques.

Lead and Other Metal Emissions

The samples of flue gas particulate collected at each site were analyzed for a total of 27 metals by Inductively Coupled Argon Emissions Plasma Spectrometry (ICAP) techniques. Lead and zinc were present at concentrations substantially higher than any other trace metals. The lead concentrations in the flue gas samples ranged from 5,380 $\mu g/m^3$ to 72,400 $\mu g/m^3$, corresponding to an average emission rate of 0.12 lb/hr. Calculations based on simplified models have shown in some cases, lead emissions at these levels could cause violations of ambient air quality standards for lead. The concentrations of zinc in the flue gas ranged from 3,100 to 34,000 $\mu g/m^3$, corresponding to an average emission rate of 0.06 lb/hr. The ratio between lead and zinc emissions was generally 2:1, consistent with their concentration in base stock oil, which was 1,550 ppm and 760 ppm by weight, respectively. Lead and zinc compounds are commonly found in waste automotive oil and result from both gasoline and oil additives.

Mass flow calculations indicated that 50-60 percent of the lead and chloride introduced into the boilers exits from the system in the flue gas. An additional 10-15 percent appears in ash collected in the firetubes of the boilers.

Other metals which received special attention were arsenic, cadmium and chromium. These were generally at low enough concentrations in the stack gas so that when diluted in the atmosphere they should not cause major problems, but the situation is still of some concern as the concentration of these metals could be substantially higher in other waste oil base stocks.

The results of metal emissions are summarized in Table 3.

Particulate and Chloride Emissions

Particulate emission rates at the six sites ranged from 0.07 to 1.2 lb/hr with an average value of 0.73 lb/hr (0.34 lb/10^6Btu heat input). This is significantly higher than the literature value of 0.09 lb/10^6Btu for commercial boilers firing residual oil,[3] but the higher value is consistent with the much higher ash content of waste oil, which can range from 0.15 to 1.5 percent. Particulate sizing measurements conducted at four of the test sites indicated that 80 to 90 percent of the particulates containing lead are submicron in nature and would be readily inhalable.

The flue gas emissions of HCl from the six boilers averaged 2.6 lb/hr. This is a relatively high emission rate for such small units, but it is below the 4.0 lb/hr air emission standard established for hazardous waste incinerators, which would typically burn large quantities of chlorinated compounds similar to those used in this program.

Products of Incomplete Combustion

The flue gas samples from each site were screened by Gas Chromatograph/Mass Spectrometer(GC/MS) for additional organic components, considered to be potential products of incomplete combustion. The types of compound which were identified are shown in Table 4. In general, the components were nonchlorinated in nature and were representative of the types of compounds that result from the combustion of traditional fossil fuels.[3,4] These compounds were also very typical of contaminants sometimes found on the blank sample adsorbing medium, XAD-2 resin. The extent to which these compounds, when detected, resulted from combustion byproducts or from resin contaminants could not be determined; hence, the concentrations in Table 4 could be viewed as upper limits for many of the nonchlorinated products of incomplete combustion. During the course of this program there were some baseline runs done on conventional No. 4 fuel oil. As expected, no chlorinated hydrocarbons were detected in the stack gas, with detection limits being 8 $\mu g/m^3$. With conventional No. 4 oil, combustion products such as naphthalene and similar polyaromatic hydrocarbon (PAH) compounds were 100 $\mu g/m^3$ or less.

Chlorinated dibenzofuran (PCDF) or chlorinated dioxin (PCDD) species were detected in 15 of the 25 samples analyzed. The concentration of these compounds ranged from 0.07 to 17 $\mu g/m^3$. On a v/v basis, this corresponds to a range of 7 to 470 parts per trillion (ppt).

Bulk samples of firetube ash collected at one of the sites contained parts per billion levels of 11 PCDF and PCDD isomers on a weight by weight basis. Because chlorinated dioxins and chlorinated dibenzofurans were found in the flue gas, tests were also conducted on the waste oil base stock, both spiked and unspiked to determine the extent to which these types of compounds might be present in the oil. No chlorinated dioxins or chlorinated dibenzofurans were found in either the spiked or unspiked oil at detection limits which were 0.2 milligrams per kilogram (mg/kg) for the tetrachlorodibenzodioxin and as low as 0.04 mg/kg for the monochlorodibenzodioxin. The same detection limits were achieved for the chlorinated dibenzofurans.

CONCLUSIONS

Although a sample population of six boilers is very limited, there do seem to be several general conclusions which can be reached regarding the combustion of waste automotive fuels in boilers in this size range.

1. It is possible to achieve combustion efficiencies greater than 99.9 percent for small commercial boilers firing waste oils.

2. Destruction and removal efficiencies of greater than 99.9 percent can be obtained for chlorinated organic contaminants typically present in waste oils. For the volatile compounds studies (Chloroform, trichloroethylene, trichloroethane and perchloroethylene), destruction and removal efficiencies were on the order of 99.9 percent. For the semivolatile compounds,)trichlorobenzene, dichloronaphthalene, trichlorophenol), destruction and removal efficiencies were on the order of 99.95 percent.

3. For boilers above 1 X 10^6 Btu/hr input, there were no apparent correlations between boiler size or firing method and destruction efficiency of organic contaminants.

4. Inorganic components, as opposed to organic components of waste oil, have substantially greater mass emission rates to the atmosphere as a result of the combustion of automotive waste oils. The principal inorganic components of concern are lead, hydrochloric acid and total particulate. Also of potential concern are arsenic, cadmium and chromium. The particulate lead emissions from a source may, during the peak heating season, affect the compliance with the primary ambient air standard for lead. A significant percentage of the particulate lead emissions is submicron in nature and would be readily inhalable.

5. Detectable levels of emissions of polychlorinated dibenzofurans and polychlorinated dibenzodioxin compounds were found in some of the boilers tested. These compounds, when present, were usually at levels less than 5 $\mu g/m^3$, which is less than 0.5 part per billion by volume in the stack gas. The extent to which these compounds pose a hazard at these low levels is undetermined.

Tests were done on the base stock waste oil, with and without the spiked contaminants, to determine the extent to which the oil may have contained trace levels of dioxin. No dioxin or dibenzofuran compounds were detected in any of the oil samples; detection limits were 200 ppb by weight for TCDD and TCDF. If dioxin compounds were present at or below their detection limits, such a quantity would not be large enough to account for the observed levels in the stack gas even with zero percent destruction. The conclusion is that dioxin and dibenzofuran found in the stack gas most probably was formed during the combustion process.

6. The fly ash deposited in the firetubes of the boilers may contain percent levels of lead and parts per billion levels of chlorinated dibenzofuran and dioxin compounds. The ash has the potential for being classified as hazardous on this basis, and may be subject to hazardous waste regulations for disposal.

ACKNOWLEDGEMENTS

This work was done under contract to the U.S. Environmental Protection Agency by GCA Corporation under Contract No. 68-02-3168. The authors would like to thank our Project Officers, Mr. Harry Freeman of EPA's Industrial and Environmental Research Laboratory in Cincinnati and Mr. Mike Petruska of EPA's Office of Solid Waste in Washington, DC for their direction and support. Mr. George Huffman of EPA's Industrial and Environmental Research Laboratory also provided important technical direction in the early stages of the program.

TABLE 1. CALCULATED DESTRUCTION AND REMOVAL EFFICIENCIES (PERCENT)

	A	C	D	E	F	G	Average by Compound
Volatile Compounds							
Chloroform	99.65	99.91	99.96	99.90	99.94	99.95	99.88
Trichloroethane	99.78	99.95	99.97	99.37	99.80	99.93	99.80
Trichloroethylene	99.45	99.92	99.89	99.85	99.92	99.87	99.82
Perchloroethylene	99.74	99.91	99.86	99.73	99.85	99.96	99.84
Semivolatile Compounds							
Trichlorobenzene	99.84	99.98	99.96	99.90	≥99.96	99.89	>99.92
Dichloronaphthalene	99.95	99.95	99.95	≥99.94	99.98	99.92	>99.95
2,4,5-Trichlorophenol	>99.97	>99.99	---	≥99.92	≥99.98	---	>99.97

TABLE 2. AVERAGE FLUE GAS CONCENTRATIONS OF THE VOLATILE AND SEMIVOLATILE SPIKE COMPONENTS

	($\mu g/m^3$)					
Site	A	C	D	E	F	G
Volatile Components						
Chloroform	110	120	44	53	88	153
Trichloroethane	90	88	22	580	400	140
Trichloroethylene	160	94	66	62	70	200
Tetrachloroethylene	160	200	180	220	170	100
Semi-Volatile Components						
Trichlorobenzene	48	20	75	51	48	89
Dichloronaphthalene	16	12	22	23	36	89
Trichlorophenol	10	9	--	16	6	--

TABLE 3. CONCENTRATIONS OF METALS IN FLUE GAS

	($\mu g/m^3$)					
Site	A	C	D	E	F	G
Arsenic	11.2	655	26.1	106	251	286
Cadmium	31.2	102	8.3	182	350	81
Chromium	62.2	166	112	230	205	263
Lead	9,680	72,400	5,390	20,300	49,800	51,000
Zinc	5,150	33,700	3,134	12,100	26,800	27,000

TABLE 4. EXAMPLES OF CONCENTRATION RANGES FOR POSSIBLE PRODUCTS OF INCOMPLETE COMBUSTION

	($\mu g/m^3$)					
Site	A	C	D	E	F	G
Naphthalene[a]	--	30	70	10	40	50
Benzaldehyde[a]	10-60	--	20-70	30	40	20
Chlorobenzene isomers	--	20	--	10	40	--
Dibenzofuran	70	5	2	10	20	5
Ethylbenzene	--	--	2-20	--	--	--
Chlorotoluene	9[b]	--	70[b]	--	--	--
Benzoic acid[a]	70	--	20-200	200	300	90
Alkyl benzene[a]	60	--	10-100	100-600	--	300

---

[a] This compound is a known contaminant of XAD-2 resin and could be a sampling and analysis artifact as well as a product of incomplete combustion.

[b] At sites A and D, chlorotoluene was not spiked into the waste oil; hence, its appearance here is as a product of incomplete combustion.

Note:

The symbol -- means the compound was not detected by mass spectrometric computer matching scan. In such cases, the detection limit is generally 100 $\mu g/m^3$ or less.

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DEMONSTRATION OF WET AIR OXIDATION OF HAZARDOUS WASTE

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ABSTRACT

The purpose of this paper is to summarize the full scale demonstration of Wet Air Oxidation of hazardous waste. This work is being done at Casmalia Resources Management, a commercial waste treater in California.

The report will summarize bench scale waste screening tests completed to date, as well as report the results of full scale oxidation of six specific wastes. Detailed analysis including Gas Chromatograph/Mass Spec (GCMS) scans of feed and effluent will be given. Wastes tested include cyanide wastes, phenolic wastes, sulfide wastes, non-halogenated pesticides, solvent still bottoms and a general organic wastewater.

Preliminary screening tests and the full scale work will be collated such that predictions might be made for the various groups of compounds.

INTRODUCTION

Wet Air Oxidation is a process which has been used to oxidize dissolved or suspended organic substances at elevated temperatures and pressures. The process is thermally self-sustaining with relatively low organic feed concentrations and is therefore most useful for wastes which are too dilute to incinerate economically yet too toxic to treat biologically.

The process has been used to treat various wastes over the last thirty to forty years. With the recent attention being focused on hazardous waste, much interest has been expressed in the use of Wet Air Oxidation as a means of destroying and/or detoxifying these hazardous wastes. During the recent years much bench scale (5)(4) and pilot plant (2) testing has been performed by various companies to demonstrate the applicability of Wet Air Oxidation on various hazardous organic wastes. Wet Air Oxidation units currently detoxify specific waste streams at several generators (1).

In this project, a 10 gallon per minute (gpm) skid mounted Wet Air Oxidation is used. This unit is located at Casmalia Resources, a commercial waste treater in California. Casmalia Resources is using the unit to process those acutely hazardous wastes which have been banned from landfilling by order of the State of California.

Wastes selected from classified groups of organic wastes have been detoxified. These groups include cyanide wastes, phenolic wastes, sulfide wastes, non-halogenated pesticides, solvent still bottoms and general organic wastewaters. Wastes supplied by generators in the South West United States are being tested.

Preliminary autoclave Wet Air Oxidation tests are run to insure compatibility and treatability with the full scale unit. Operating conditions are also established with these tests. A continuous test of a minimum of eight hours is completed with the full scale unit.

PURPOSE

The purpose of this test is to demonstrate Wet Air Oxidation of toxic and hazardous wastes at a full scale installation. Data has been developed on a commercial scale, continuous unit. Wastes tested were those actually produced by industrial clients in the South West portion of the United States. Results will be collated such that predictions might be made for all the compounds of particular classes.

APPROACH

The Zimpro Wet Air Oxidation unit (see Figure 1), processes aqueous wastes at a designed reactor temperature of 280°C, a designed reactor pressure of 136 atmosphere (atm) and a liquid waste flow rate of 2.3 cubic meters per hour (m^3/hr) (10 gpm). Waste is pressurized, mixed with compressed air, and directed through the cold, heat-up side of the heat exchanger. The incoming waste-air mixture exits from the heat-up side of the heat exchanger and enters the reactor where exothermic reactions increase the temperature of the mixture to a desired value. The waste-air mixture exits the reactor and enters the hot, cool-down side of the heat exchanger and, after passage through the system pressure control valves, is directed to the separator. In the separator, the spent process vapors (non-condensible gases) are separated from the oxidized liquid phase and are directed into a two-stage water scrubber-carbon bed adsorber, vapor treatment system.

In the Wet Air Oxidation process, organic substances can be completely oxidized to yield highly oxygenated products and water. For example, organic carbon-hydrogen compounds can be oxidized to carbon dioxide and water, while reduced organic sulfur compounds (sulfides, mercaptans, etc.) and inorganic sulfides are easily oxidized. It should be noted that oxides of nitrogen such as NO or NO_2 are not formed in Wet Air Oxidation because reaction temperatures are not sufficiently high to form them.

When incomplete oxidation of organic substances occurs, the easily oxidized sulfur and cyanide compounds are usually still oxidized to sulfate and carbon dioxide-ammonia provided a sufficient degree of oxidation is accomplished. However, incomplete oxidation of other organic compounds results in the formation of low molecular weight compounds such as acetaldehyde, acetone, and acetic acid. These low molecular weight compounds are volatile and are distributed between the process off-gas phase and the oxidized liquid phase. The concentration of these low molecular weight compounds (measured as total hydrocarbons (THC) expressed as methane) in the process off-gas is dependent on their concentration in the oxidized liquid phase, which is determined by the degree of oxidation accomplished; the waste being oxidized; and the influent organic concentration of the waste.

Autoclave Screening

In this project, wastes were prescreened using autoclave (Photo 1) Wet Air Oxidation tests. These bench scale tests generally demonstrate the level of destruction or detoxification expected. Corrosion tests were also conducted to insure compatibility with the full scale unit.

Raw and oxidized samples were analyzed for chemical oxygen demand (COD), biological oxygen demand (BOD), pH, total solids, ash, soluble chloride, soluble fluoride and specific component, e.g. cyanide, phenol, sulfide, pesticide or solvent. The condensible off-gas from the autoclave was analyzed for oxygen, nitrogen, carbon dioxide, total hydro-carbon and methane. The autoclave and oxidized liquid effluent was examined for any residue which might cause heat exchanger fouling or plugging of the full scale unit.

Full Scale Testing

Each waste was tested during a one (1) day "demonstration period", to determine the effectiveness of the Wet Air Oxidation unit. During each "demonstration period", the sampling and testing program outlined as follows was used.

Upon arrival of a truckload of a screened and acceptable waste, a sample of the waste was obtained and analyzed for COD, pH, and specific component.

During the Wet Air Oxidation of each class of waste, liquid composites of the influent raw waste and the effluent oxidized waste were obtained. Liquid samples of these two streams were made on an hourly interval and the liquid samples were composited over a 24 hour period or throughout the steady-state operation of the Wet Air Oxidation unit, if operated less than 24 hours per day. Split samples were made with one sample going to the State laboratory and the other going to Zimpro's laboratory for analyses. The raw waste and oxidized waste were each analyzed for COD, BOD, pH, total solids, ash, soluble chloride, soluble fluoride and specific component, e.g., cyanide, phenols, sulfide, chlorinated aliphatic compounds, or non-halogenated pesticide. In addition, the oxidized waste were also analyzed for dissolved organic carbon (DOC) and a GCMS scan was made.

Grab samples of off-gas from the Wet Air Oxidation unit, sampled after treatment but prior to discharge to the atmosphere, were made in Tedlar gas sampling bags.

The sample of Wet Air Oxidation process off-gas was analyzed for oxygen, nitrogen, carbon dioxide, carbon monoxide, total hydrocarbon, and methane. Gas sampling was conducted when the Wet Air Oxidation unit was operating at steady-state. Two replicate grab samples were obtained each day that the waste were processed in the Wet Air Oxidation unit during the "demonstration period". The samples were analyzed by the State.

PROBLEMS ENCOUNTERED

Several problems were encountered during this project. The most serious were the delays in obtaining necessary permits to operate the unit. This resulted in the obvious delays in start-up. Once running, it was necessary to process the available wastes being brought to the site. The owner did not wish to run specific wastes with the added sampling procedures, when wastes were available for commercial treatment.

A major portion of the wastes processed has been plating wastes. With the destruction of the cyanide and other organic complexing agents, metal oxides and hydroxides tend to precipitate. Adjustments in the operating procedures and conditions were necessary to prevent excess fouling and solids deposition.

All classes of wastes to be tested have been actual wastes except for the pesticide waste. After searching for over a year, it has been necessary to synthesize that waste.

RESULTS

Autoclave Screening Tests

Table 1 lists results of autoclave screening tests. Corrosion tests showed that all wastes listed were shown to be compatible with the materials of construction of the full scale units. Most wastes rejected in the prescreening process were rejected due to a high corrosion rate. Note that prescreening of wastes through review of chemical analysis kept the number of unsuccessful autoclave screenings to a minimum.

Full Scale Testing (3)

Tables 2, 3, and 4 show the results for full scale testing. Each table lists the results of a particular class of waste. At the time of submission, complete off-gas data was not available but Tables 5, 6, and 7 show results for those tests completed.

Destruction of cyanide was greater than 99.7%. Effluent cyanide was 82 mg/l with a feed of 25,390 mg/l. The phenol waste oxidation resulted in 99.77%, destruction with an effluent of 36 mg/l and a feed of 15,510 mg/l. Organic sulfur destruction reached 94% with feed and effluent concentrations of 3010 mg/l and 180 mg/l. In the general organics wastewater test dissolved organic carbon (DOC) destruction was 96.7% with feed and effluent concentrations of 20,830 mg/l and 685 mg/l.

While all waste processing runs have been completed, complete analytical data is not available at time of publication.

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TABLE 1. AUTOCLAVE TESTS - CASMALIA RESOURCES
Test Conditions - 280°C, 1 Hr. Reactor Residence Time

Waste	Parameter	Feed	Effluent	% Removal
Spent Caustic	COD, g/l	40.0	7.5	81.3
	Total Phenols, mg/l	5350	66	98.8
	Sulfide, mg/l	382	< 1	>99.7
Acid Distillate	COD, g/l	40.1	5.8	85.5
Alkaline Solvent	COD, g/l	39.8	7.5	81.2
	Total Phenols, mg/l	840	20	97.6
Cyanide Plating	COD, g/l	17.1	3.2	81.3
	Cyanide, mg/l	6910	120	98.3
Metal Finishing Cyanide	COD, g/l	40.4	6.0	85.1
	Cyanide, mg/l	5090.0	36.0	99.3
Cyanide Plating	COD, g/l	40.2	8.6	78.6
	Cyanide, mg/l	20960.0	234.0*	98.9
Pesticide Rinsate	COD, g/l	20.0	4.1	79.5
	Organic N, mg/l	701.0	156.0	77.7
Cadmium Plating	COD, g/l	11.3	3.6	68.1
	Cyanide, mg/l	12980.0	52.0	99.6
Solvent Still Bottoms	COD, g/l	43.9	8.6	80.4
	BOD, g/l	21.3	6.3	70.4
	BOD/COD	.49	.74	--
Rocket Fuel Waste Mixture	COD, g/l	45.1	1.8	96.0
Cyanide Wastewater	COD, g/l	29.6	10.4	64.9
	Cyanide, mg/l	33160.0	185.0	99.4
Pesticide Wastes	COD, mg/l	1640.0	450.0	72.6
	BOD, mg/l	15.0	208.0	--
	BOD/COD	0.01	.46	
Pesticide	COD, g/l	5.38	.85	84.2
	BOD, g/l	1.81	.725	53.0
	BOD/COD			

* During continuous operation a full scale unit, oxidized product contained less than 7 ppm cyanide or >99.96% destruction.

TABLE 2. WET AIR OXIDATION DEMONSTRATION OF GULF OIL SPENT CAUSTIC WASTEWATER

Wet Air Oxidation Conditions:

Oxidation Temperature	515°F (268°C)
Nominal Residence Time	113 min.
Waste Flow Rate	5.3 GPM
Compressed Air Flow Rate	190 SCFM
Reactor Pressure	1610 PSIG
Residual Oxygen Concentration	3.7%

Sample Description	Composite Influent Raw Waste	Composite Effluent Oxidized Waste
COD, g/l	108.1	11.6
COD Reduction, %	--	89.3
Total Phenols, mg/l	15,510	36
Total Phenols Reduction, %	--	99.77
Total Sulfur, mg/l	3580	3090
Sulfate Sulfur, mg/l	570	2910
*Organic Sulfur, mg/l	3010	180
Organic Sulfur Reduction, %	--	94.0
Sulfide Sulfur, mg/l	<1.0	<1.0
pH	13.0	8.3
Total Solids, g/l	88.6	59.7
Total Ash, g/l	57.1	50.2
Volatile Solids, g/l	31.5	9.5
DOC, mg/l	--	3680
Soluble Chloride, mg/l	1510	550
Soluble Fluoride, mg/l	4.4	1.3

*Organic Sulfur - Total Sulfur Minus Sulfate Sulfur

TABLE 3. WET AIR OXIDATION DEMONSTRATION CYANIDE WASTEWATER CLASS

Wet Air Oxidation Conditions:

Oxidation Temperature	495°F (275°C)
Nominal Residence Time	80 min.
Waste Flow Rate	7.5 GPM
Compressed Air Flow Rate	190 SCFM
Reactor Pressure	1220 PSIG
Residual Oxygen Concentration	7.1%

Sample Description	Composite Influent Raw Waste	Composite Effluent Oxidized Waste
COD, g/l	37.4	4.2
COD Reduction, %	--	88.8
Cyanide, mg/l	25,390	82
Cyanide Reduction, %	--	99.7
DOC, mg/l	14,710	1710
DOC Reduction, %	--	88.4
pH	12.6	9.0
Total Solids, g/l	135.3	91.2
Total Ash, g/l	112.9	77.4
Volatile Solids, g/l	22.4	13.8
BOD_5, mg/l	--	603
Soluble Chloride, mg/l	--	773
Soluble Fluoride, mg/l	30	29

TABLE 4. WET AIR OXIDATION DEMONSTRATION GENERAL ORGANIC WASTEWATER CLASS

Wet Air Oxidation Conditions:

Oxidation Temperature	531°F (277°C)
Nominal Residence Time	120 min.
Waste Flow Rate	5.0 GPM
Compressed Air Flow Rate	190 SCFM
Reactor Pressure	1515 PSIG
Residual Oxygen Concentration	4.1%

Sample Description	Composite Influent Raw Waste	Composite Effluent Oxidized Waste
COD, g/l	76.0	2.5
COD Reduction, %	--	96.7
DOC, mg/l	20,830	685
DOC Reduction, %	--	96.7
pH	1.9	3.3
Total Solids, g/l	10.0	3.1
Total Ash, g/l	0.7	1.1
Volatile Solids, g/l	9.3	2.0
BOD_5, mg/l	29,680	880
BOD_5/COD, g/g	0.39	0.35
Soluble Chloride, mg/l	212	866
Soluble Fluoride, mg/l	0.7	<0.5

TABLE 5. WET AIR OXIDATION DEMONSTRATION SPENT CAUSTIC WASTEWATER (PHENOL & SULFIDES)

Process Off-Gas Analysis	
Carbon Dioxide	11.3%
Oxygen	4.3%
Nitrogen	83.2%
Carbon Monoxide	Not Detected
Methane	12.1 ppm
Total Hydrocarbons	85.4 ppm as methane

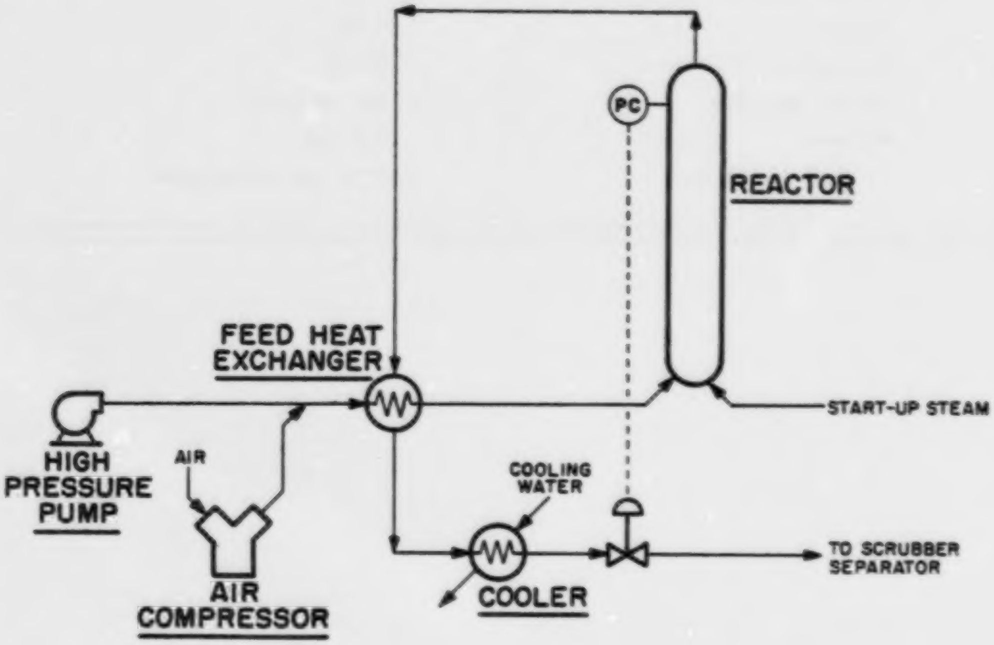
TABLE 6. WET AIR OXIDATION DEMONSTRATION CYANIDE WASTEWATER CLASS

Process Off-Gas Analysis	
Carbon Dioxide	1.5%
Oxygen	8.5%
Nitrogen	82.8%
Carbon Monoxide	Not Detected
Methane	9.0 ppm
Total Hydrocarbons	61.1 ppm as methane

TABLE 7. WET AIR OXIDATION DEMONSTRATION
GENERAL ORGANIC WASTEWATER CLASS

Process Off-Gas Analysis	
Carbon Dioxide	12.9%
Oxygen	5.9%
Nitrogen	81.2%
Carbon Monixide	0.3%
Methane	10.0 ppm
Total Hydrocarbons	29.1 ppm as methane

FIGURE I. WAO ELEMENTARY FLOW SHEET


PC
REACTOR
FEED HEAT EXCHANGER
START-UP STEAM
HIGH PRESSURE PUMP
AIR
COOLING WATER
AIR COMPRESSOR
COOLER
TO SCRUBBER SEPARATOR

EVALUATION OF PILOT-SCALE APCDs FOR HAZARDOUS WASTE COMBUSTION SOURCES

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ABSTRACT

Conventional air pollution control devices used at hazardous waste combustion facilities may not adequately control fine particulate matter and some gaseous species. This project sought to identify alternate technologies that might provide a higher degree of control. The performance characteristics of several alternate technolgies is to be tested at a full-scale incineration facility. This paper is an interim report on the project.

INTRODUCTION

Combustion of hazardous waste compounds can potentially generate particulate and gaseous emissions that may have adverse health effects on exposed populations. Conventional control devices are of varying effectiveness in controlling these emissions. Wet scrubbers are often used to remove both particulate and gaseous contaminants in the same device. Wet scrubbers, however, tend to remove large particles more efficiently than they remove small particles, and at high collection efficiencies they require more energy than do electrostatic precipitators (ESPs) or fabric filters. These performance characteristics allow the escape of noxious fine particulate matter into the atmosphere from hazardous waste combustion sources.

Advanced devices are expected to be marketed with higher collection efficiency, lower energy consumption, or lower cost than current conventional types of equipment. It is likely that some of these devices are capable of providing better emission control than is now available for hazardous waste combustion products.

In Phase I of this project, RTI assessed the current state of development of devices that have the potential to control emissions from hazardous waste combustion sources and recommended a number for field testing. Phase II of the project consists of testing several of these units on a slip-stream from a hazardous waste incineration facility.

Currently, Phase I of the project has been completed. Phase II, Field Testing of the Units Selected, has just begun. This paper describes the work completed to date.

PURPOSE

The purpose of this project is to identify technologies that are potentially superior to air pollution control devices (APCDs) that are in current use for controlling emissions from hazardous waste combustion facilities and to test the performance of these technologies on commercial-scale combustion facilities.

APPROACH

The project is being conducted in several phases. In Phase I, the currently used technologies and the potentially superior technologies under development were identified. The potentially superior technologies were identified by contacts with vendors, research organizations, literature reviews, and communication with experts in the field. Both technologies that have been used on other combustion sources, but not widely used at hazardous waste combustion facilities, and technologies at various stages of development from bench-scale to pilot-scale were evaluated. The primary factor considered in the evaluation was potential applicability for controlling submicron particulate matter and/or HCl emissions. Secondary factors considered were the potential for reduced operating costs and reduced environmental impacts of the discharge from the devices.

After identification of the technologies that seemed to have the greatest potential for controlling emissions from hazardous waste combustion facilities, efforts were undertaken, through direct contact with the developer/marketer of the technology, to ascertain if pilot units of suitable size and construction either existed or could be fabricated. If the unit existed, discussions were initiated to determine if the developer/marketer would be interested in participating in testing of the unit at a hazardous waste combustion facility.

Concurrent with this latter activity, discussions were initiated with several commercial hazardous waste incineration facilities to solicit their interest and cooperation in allowing tests of the selected pilot units at their facility. Scheduling was coordinated with all involved parties to provide sufficient time for testing, yet not unduly inconvenience the host incineration facility.

PROBLEMS ENCOUNTERED

Few problems were encountered in Phase I of this project. However, RTI recognizes that some innovative devices in current commercial use may not have been identified. A detailed investigation of all facilities was not undertaken and some facilities having custom-designed equipment may have been unwilling to discuss what might be considered competitive advantages. RTI also recognizes that it is possible that not all innovative new technologies were discovered in this investigation. Technologies that had not been publicized or that were not reasonably well-known to researchers in this field would have been overlooked.

More significant problems were encountered in Phase II, Field Testing, that had an impact on timely completion of the project. These difficulties arose both in obtaining units to test and in finding a suitable host plant at which to conduct the tests.

In Phase I, we had identified a number of technologies meriting demonstration testing. Our study required that mobile pilot units having capacities of 1,000 to 4,000 cubic feet per minute of stack gas be available. These were not available for all technologies. Secondly, the study would compare the performance of all tested APCDs on the same source. Some APCD developers were unwilling to participate under these constraints, perhaps because they did not feel their test unit had yet achieved its potential. Among the APCD developers who did wish to participate, a few more mundane problems arose. These included negotiating the financial arrangement and coordination of test schedules.

Delays were also encountered in locating a suitable host plant for the study. Our first choice, who had expressed a strong interest in participating, encountered difficulties with regulatory authorities and, after much delay, had to withdraw. An alternative facility was sought which met the following criteria: regulatory authorities will allow the test, the facility is burning the appropriate type of waste (contained significant amounts of ash and chlorine), the facility design is such that a slip-stream of gas could safely be taken prior to the plant's emission control system, the facility management is willing to allow the testing, acceptable schedules, and financial arrangements could be made.

As a result of the difficulties cited above, a significant schedule delay was encountered. However, field testing of the first pilot unit did commence in March 1984.

RESULTS

In this section, we describe some of the results of this project. However, since the field testing phase has just begun, no test results can be provided.

Current Technologies

As might be expected, the principal generic types of APCDs in current use are wet scrubbers, baghouses, and electrostatic precipitators. Wet scrubbers, which have the capability of controlling both particulate and gaseous components, predominate. Fine particulate matter is generally captured poorly, and many facilities have a difficult time consistently meeting regulatory requirements.

Advanced Devices

A partial listing of the advanced

APCDs identified in Phase I is given in Table 1. The three principal types (ESPs, wet scrubbers, dry scrubbers) are listed by the company marketing the device. Where appropriate, the type of device is given.

TABLE 1. ADVANCED DEVICES

ESPs

Beltran Inc. and Micropul, Inc.
(Wet Type)

Wet Scrubbers

Lone Star Steel
(Steam Hydro and Free Jet)
Ceilcote, Inc.
(Ionizing)
University of Washington
(Electrostatic Spray)

Dry Scrubbers

Micropul/Koch
Niro Atomizer, Inc.
ETS, Inc.
Rockwell International

Wet ESPs have been around for sometime but have not been widely used on hazardous waste combustion facilities. In these devices, particulate collection is by electrostatic forces. Collected particulates are removed with a water spray. This reduces re-entrainment problems from high resistivity particles.

The Lone Star Steel wet scrubbers shown in Figure 1 use steam or air to produce very finely atomized water droplets which contact the particulate matter, resulting in an increase in the apparent diameter. Removal can then be accomplished easily with a cyclone separator.

The Ceilcote ionizing jet scrubber shown in Figure 2 precharges the particulate entering the scrubber. Fine particulate adheres to the packing materials by induced polarization and is removed by the water spray. The electrostatic spray scrubber developed at the University of Washington carries this concept one step further by also applying a charge to the water spray.

The discharge from all of the dry scrubbers is a dry powder. Each differs in the technology for introducing the gas scrubbing medium, however. Most of these units atomize a caustic (lime or sodium carbonate) slurry into the gas stream and use the heat content of the gas to evaporate the moisture. The ETS, Inc. unit shown in Figure 3, however, injects a dry powder (either lime or nacholite).

Devices Selected for Testing

At this point, arrangements have been made to test four pilot APCDs. These are the two versions of the Lone Star Steel scrubbers, the Ceilcote, Inc. unit, the ETS, Inc. unit, and the Hi-Tac unit developed by Vulcan Engineering Company. Th Hi-Tac unit, which has not been mentioned previously, is a specially designed baghouse that can operate at temperatures up to 1300°F.

Each of these are mobile pilot units that have capacities within the range of 1,000 to 4,000 cubic feet per minute of stack gas.

Host Plant for Testing

ENSCO, Inc. agreed to participate in testing the selected pilot units at their El Dorado, Arkansas incinerators complex. At this facility, oils and capacitors containing polychlorinated biphenyls (PCBs) are incinerated. Duct work has been installed to remove a slip-stream of gas from the system immediately upstream of the emission control system. Provision has been made to cool the gas to the temperatures required by the various pilot units.

Test Methods

Simultaneous inlet and outlet testing is scheduled for each unit. The testing is comprised of particle size determinations (by impactor), total particulate concentration (by EPA Method 5), and HCl concentration (by adsorption is back half of Method 5 train). Three Method 5 particulate/HCl tests are conducted each day. One particle size determination per day is made. A 2-week test period is allotted for each unit.

Test Results

Field testing has just been completed on the first pilot unit (provided by Lone Star Steel). Preliminary data indicate the unit achieved excellent removal of both fine particulate and HCl. The data, however, have not been subjected to a thorough review at this time. In our opinion, it is inadvisable to publish data under these conditions.

ACKNOWLEDGMENTS

This project is being conducted under EPA Contract No. 68-03-3149, Work Assignments 12-1, 12-4, and 12-9. Harry Freeman, IERL/Cincinnati, is the EPA Project Monitor. Engineering Science, Inc., is conducting the onsite testing under a subcontract to RTI.

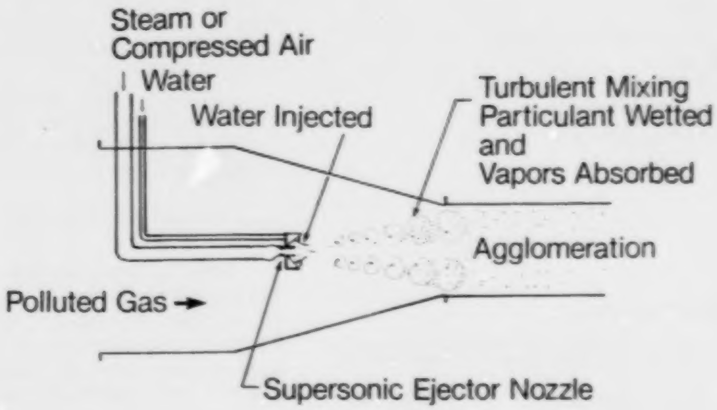
Steam or
Compressed Air
Water
Water Injected
Turbulent Mixing
Particulant Wetted
and
Vapors Absorbed
Agglomeration
Polluted Gas →
Supersonic Ejector Nozzle

Figure 1. Ejector Drive for Steam-Hydro Scrubber

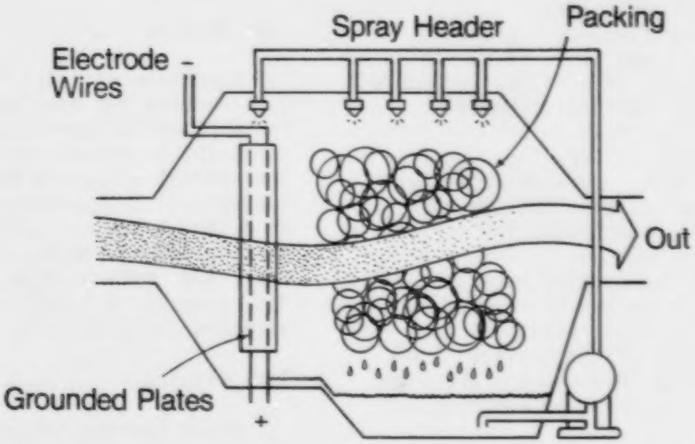
Spray Header
Packing
Electrode -
Wires
Out
Grounded Plates
+

Figure 2. Ceilcote Ionizing Wet Scrubber

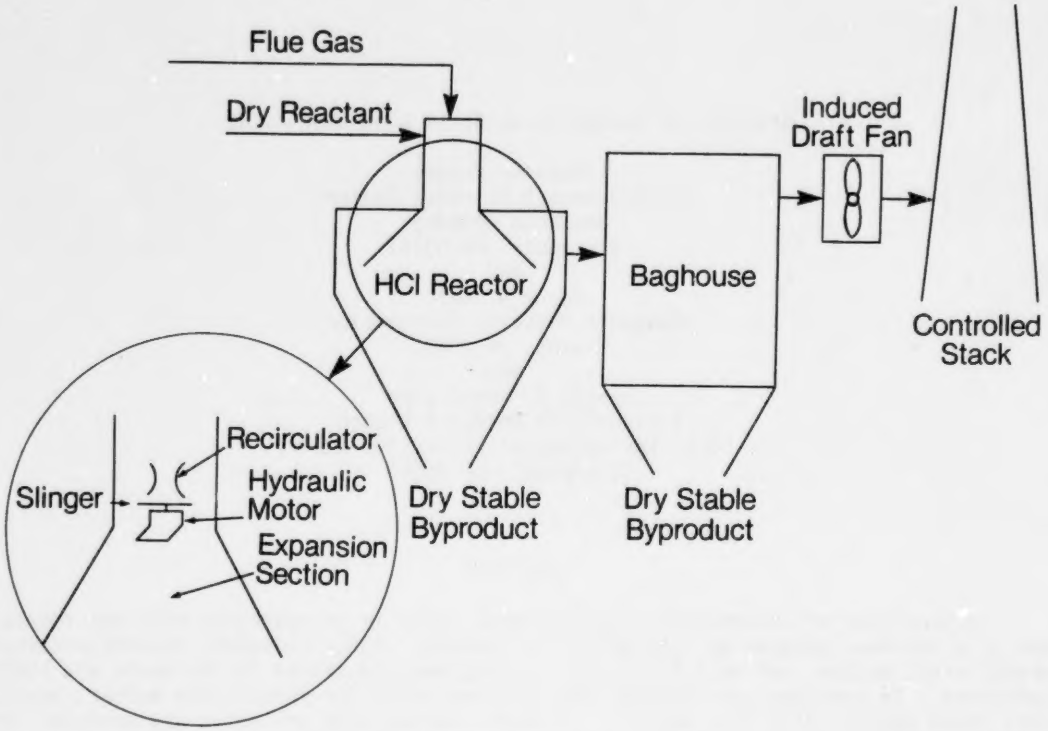
Flue Gas
Dry Reactant
HCl Reactor
Baghouse
Induced Draft Fan
Controlled Stack
Recirculator
Hydraulic Motor
Slinger
Expansion Section
Dry Stable Byproduct
Dry Stable Byproduct

Figure 3. ETS Dry Reactor

DISPOSAL OF HAZARDOUS WASTE IN AGGREGATE KILNS

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ABSTRACT

Incineration of chlorinated liquid organic waste in an aggregate kiln was investigated in a one-week program at Florida Solite Company. POHCs (toluene, tetrachloroethylene, methyl ethyl ketone, and methyl isobutyl ketone) were monitored in the waste and stack emissions. In addition, stack emissions were monitored for particulate matter, particulate trace metals, HCl, SO_2, and NO_x. Process samples were collected and analyzed for trace metals and chlorine. The destruction and removal efficiency of POHCs and the fate of trace metals and chlorine in the kiln process were determined.

Consistent achievement of greater than 99.99% DRE was demonstrated for each POHC. Emissions of other pollutants ranged as follows: particulates - 4.4 to 6.5 kg/hr; HCL - 0.008 to 0.034 kg/hr; SO_2 - 72.2 to 99.6 kg/hr; NO_x - 1.9 to 11.7 kg/hr. Between 60 and 90% of the chlorine is fed to the kiln from the waste fuel and scrubber influent water. Over 95% of the chlorine is removed from the kiln in the scrubber effluent water.

INTRODUCTION

Cofiring of hazardous wastes in high temperature industrial processes is an attractive alternative to hazardous waste incineration because it utilizes the waste's heat content. Many cofiring processes, which include cement and dolomite kilns, glass furnaces, steel furnaces, and some industrial boilers, provide temperatures and residence times similar to those required for dedicated hazardous waste incinerators. In addition to the savings derived from the heat value, the use of existing industrial equipment does not require the capital investment required for a separate or new incinerator to dispose of a hazardous waste, and it may provide an environmentally acceptable alternative to conventional hazardous waste land disposal options.

Aggregate kilns, because of their high energy use, are an excellent example of this concept. Such kilns typically operate at temperatures over 1093°C (2000°F), have gas residence times in excess of 1.5 seconds, and have a highly turbulent combustion zone. However, the need exists for data that shows the environmental effect of cofiring hazardous waste on the emissions and effluents from the aggregate process.

Currently, the State of Florida Department of Environmental Regulation (DER), in implementing RCRA regulations, allows exemptions from hazardous waste incinerator emission standards if the facility uses the waste as a fuel for the purpose of recovering useable energy. The Florida Solite Corporation located in Green Cove Springs, Florida, petitioned the Florida DER for a change in their air pollution permit to allow the burning of organic wastes as supplemental kiln fuel, thereby recovering energy from these wastes and offsetting their use of pulverized coal. A sampling and analysis program was conducted at Florida Solite Corporation from February 20-25, 1983, when burning coal and hazardous waste as fuel. Program results will allow the Florida DER to decide whether the existing regulatory exemptions are environmentally sound and they will provide additional hazardous waste incineration data for the EPA Industrial Environmental Research Laboratory - Cincinnati.

The sampling and analysis program included evaluation of: (1) the destruction and removal efficiency (DRE) of principal organic hazardous constituents (POHCs) when cofiring coal and waste fuel; (2) the concentrations of particulate matter, SO_2, NO_x, HCl, and metals in stack emission, and (3) the concentration and fate of metals and chlorine in the process streams.

FACILITY AND PROCESS DESCRIPTION

The Florida Solite Company operates an aggregate kiln in Green Cove Springs, Florida, which is located approximately 20 miles south of Jacksonville. Annual production of the expanded lightweight inorganic material used as aggregate in a cement mix is approximately 5.45 x 10^7 kg (60,000 tons) per year.

This industrial process involves the heating of clay to a temperature of 2,000° F to 2,100°F in a horizontal rotary kiln to prepare an expanded lightweight inorganic material used as aggregate in cement mix.

The kiln, with refractory linings, is 2.7 m(9 ft) in diameter and 45.7 m (150 ft) long. The kiln rotates slowly (90 revolutions per hour) and has a gentle slope (6.25 cm/m) to allow material to pass through by gravity. The kiln operates in a counter current flow pattern; i.e., solid materials travel in one direction and hot gases and dust travel in the opposite direction, as shown in Figure 1. Clay is fed into the kiln at the upper end at a rate of approximately 12,260 kg/hr (27,000 lb/hr). At the opposite end of the kiln, a mixture of coal and waste fuel is burned at rates of approximately 700 kg/hr (1,540 lb/hr) and 0.87 m^3/hr (230 gal/hr), respectively, to provide a heat input of approximately 22,000 kw (74 million Btu/hr). As the clay feed travels down the inclined rotating kiln, it passes through various temperature ranges which cause transformation of the clay into the lightweight aggregate product. The lightweight aggregate is produced at a rate of approximately 9,080 kg/hr (20,000 lb/hr). After heating and transformation in the kiln, the aggregate is graded and large clumps are crushed for sizing. The final product is stored in large piles until sold.

The kiln exhaust gases pass through a pair of mechanical dust collectors, whose dust is recycled into the kiln, then into a horizontal cross-flow water scrubber of fiber-reinforced-plastic (FRP) construction. The series of water sprays clean the particulate matter and reduces the gas temperature from about 370° to 70°C (700°F to 160°F) before the gases reach the knockout chamber and fiberglass stack. The scrubber discharge released from the knockout chamber is a mixture of raw steam and water with the entrapped particulate matter. This discharge stream is released to an open ditch which drains to a pond. There is no recycle of the scrubber water.

The fuel used to fire the kiln is an unblended combination of crushed coal and waste organic liquids. The liquid wastes, which are trucked directly from the generators, consist primarily of solvents, alcohols, ethers, still bottoms, and a small fraction of chlorinated hydrocarbons. Any manifested wasteload that contains pesticides, PCBs, acids, caustics, cyanides, sulfides, mercaptans, electroplating wastes, or metal finishing wastes is rejected and returned to the generator. The organic waste mixture makes up from 50% to 100% of the fuel used. During the test period, the waste fuel comprised approximately 54% of the total heat input.

EXPERIMENTAL PROGRAM

The sampling and analytical program was designed to identify the major pollutants from burning waste fuel in an aggregate kiln, quantify their respective emission rates, determine the destruction and removal efficiency (DRE) of the POHCs, and provide information for a mass balance around the process for metals and chlorine. Measured stack pollutants include POHCs (toluene, tetrachloroethylene, methyl ethyl ketone, and methyl isobutyl ketone), particulate matter, particulate trace metals, carbon dioxide, hydrogen chloride, sulfur dioxide, and nitrogen oxides. In addition, the distribution of the metals and chlorine were measured in all of the process input and output streams; i.e., the coal feed, waste feed, clay feed, scrubber influent water, aggregate product, and scrubber effluent water. Waste fuel and coal samples were submitted for analyses of sulfur, ash, and Btu content. Waste fuel and scrubber effluent water also were analyzed for principal organics. Table 1 summarizes the overall test program and lists each sampling and analytical method use.

Sampling was conducted for five full test days. Because the kiln rarely operates on 100% coal fuel feed, the test was conducted on normal fuel operation (i.e., coal and waste fuel) and no baseline (coal only) testing was performed. A Quality Assurance Project Plan was reviewed and approved prior to the test program. A full description of the QA/QC results involving replicates, splits, blanks, spikes, and reference standards is provided in the final report.

RESULTS AND DISCUSSIONS

WASTE FUEL

A detailed summary of the waste fuel samples collected as shown in Table II. Table III and IV show the concentration of each POHC and other properties for the five waste fuel samples (one sample per day, Runs 1-5).

POHC Destruction and Removal Efficiencies

The complex combustion chemistry for organic materials becomes perplexing when a broad range of organic compounds present in a liquid waste are burned. On a weight basis, most of the organic carbon in the waste is oxidized to CO_2 in the combustion process, but trace amounts of organic chemicals survive the oxidation process and are partially reacted. Accordingly, the test burn investigated the amount of destruction of the organic compound in the hazardous waste.

Destruction and removal efficiency (DRE) for an incineration/air pollution control system is defined by the following equation:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} (100)$$

Where DRE = Destruction and removal efficiency, %

W_{in} = Mass feed rate of principal organic hazardous constituent (s) (POHCs) fed to the incinerator

W_{out} = Mass emission rate of principal organic hazardous constituent(s) (POHCs) to the atmosphere (as measured in stack prior to discharge).

DRE calculations are based on combined efficiencies of the destruction of the POHC in the incinerator, or the aggregate kiln in this case, and the removal of the POHC from the gas stream in the air pollution control system. The presence of POHCs in liquid/solid discharges from the air pollution control devices is not accounted for in the DRE calculation as currently defined by the EPA. RCRA Part 264, Subpart O regulations for hazardous waste incinerators require a DRE of 99.99% for all principal organic hazardous constituents of a waste unless it can be demonstrated that a higher or lower DRE is more appropriate based on human health

INPUTS	OUTPUTS
Coal	Aggregate product
Waste fuel	Scrubber effluent water
Scrubber influent water	Stack gas
Clay feed	

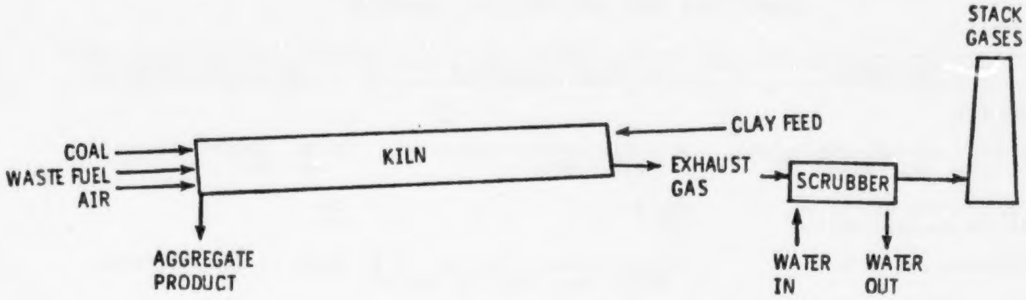


Figure 1. Schematic diagram of aggregate kiln process.

criteria. Specification of the POHCs in a waste is subject to best engineering judgment, considering the toxicity, thermal stability, and quantity of each organic waste constituent. For the selected POHCs, toluene, MEK, and Perc are RCRA Part 261, Appendix VIII compounds; MIBK is not listed. DRE requirements in the Subpart O regulations do not apply to metals or other noncombustible materials. Currently, aggregate kilns are exempt from trial burn testing.

Toluene, MEK, and MIBK were present in high concentration for organic compounds (see Table II). Perc was selected because the chlorinated hydrocarbons are, in general, difficult to thermally destroy and Perc was the only chlorinated organic measured in the top twenty constituents of the wastes fuel.

The four POHCs were sampled in the exhaust gas by the volatile organic sampling train (VOST) and analyzed by gas chromatography/mass spectrometry (GC/MS). The number of acceptable VOST runs made each day were as follows: day 1 - 0 runs; day 2 - 6 runs; day 3 - 6 runs; day 4 - 8 runs; day 5 - 5 runs. The average DRE and range obtained is shown in Table V. Figure 2 illustrates the frequency of obtaining a certain "number of nines" of DRE for each POHC.

Methyl ethyl ketone was destroyed and removed to at least 99.99% efficiency. Only three runs showed DREs less than 99.999%: Runs 4A, 3A[3] and 3B[3] were side-by-side runs (with 3A and 3B) that were split with the EPA QA contractor. Runs 3A[3] and 3B[3] do not show good comparison with Runs 3A and 3B for MEK, possibly because of blank contamination problems in the QA contractor field blanks. Run 3B[3] is an outlier and is not considered a significant part of the data. The overall DRE average for MEK for all five days was 99.998% ± 0.006% (95% confidence limits).

DREs for methyl isobutyl ketone (MIBK) ranged from 99.986% to ≥99.999%. The 99.986% value was the only DRE less than 99.992%. The overall average for MIBK was 99.998% ± 0.006% (95% confidence limits).

DREs for tetrachloroethylene (Perc) ranged from 99.993% to ≥ 99.999%. Excellent consistency was found for each day dampling. Split samples on Day 3 (Runs 3A[3], 3B[3], and 3D[1]) all showed low

TABLE 1. SUMMARY OF FLORIDA SOLITE AGGREGATE KILN SAMPLING AND ANALYTICAL PROGRAM

Parameter	Sampling method	Analytical method
Stack Gas		
· POHCs (tetrachloroethylene, toluene, MEK, MIBK)	Volatile organic sampling train (VOST)	GC/MS, thermal desorption and SIM
· Particulate matter	EPA 5	EPA 5
Metals on particulate	EPA 5	ICP
· Hydrogen chloride	Impinger absorption in 0.5 M NaoAc (back half of EPA 5)	Specific ion electrode
· CO_2 and O_2	EPA 3	Fyrite
· Nitrogen oxides	EPA 7	EPA 7
· Sulfur dioxide	EPA 6	EPA 6
Waste Fuel		
· Principal organics	Grab → composite	GC/MS
· Metals	Grab → composite	ICP
· Chlorine, sulfur	Grab → composite	XRF
· Btu content	Grab → composite	ASTM D240-64
· Ash content	Grab → composite	ASTM D482-IP4
Scrubber Discharge[a]		
· POHCs	Grab → composite	GC/MS
· Metals	Grab → composite	ICP
· Lead	Grab → composite	AAS
· Hexavalent chromium	Grab → composite	APHA312B
· Chlorine	Grab → composite	XRF
Aggregate Product		
· Metals	Grab → composite	ICP
· Chlorine	Grab → composite	XRF
Clay Feed		
· Metals	Grab → composite	ICP
· Chlorine	Grab → composite	XRF
Coal		
· Metals	Grab → composite	ICP
· Chlorine, sulfur	Grab → composite	XRF
· Btu and ash content	Grab → composite	ASTM D240-64
Scrubber Influent		
· Metals	Grab → composite	ICP
· Chlorine	Grab → composite	XRF

[a] The scrubber discharge was split into sludge and supernatant fractions and was analyzed separately where applicable.

TABLE II. RESULTS OF CAPILLARY GC/MS ANALYSIS OF MAJOR COMPONENTS OF WASTE FUELS NUMBER 1 AND NUMBER 4

Waste fuel component	Concentration, wt % Number 1[a]	Number 4[a]
Ethanol	1.55	1.83
2-Propanol	4.55	1.97
1-Butanol	1.78	0.77
Ethyl acetate	0.68	0.72
Methyl ethyl ketone (POHC)	2.03	2.81
Methyl isobutyl ketone (POHC)	1.52	1.12
Toluene (POHC)	8.40	8.06
Tetrachloroethylene (POHC)	0.19	0.07
Ethylbenzene	1.23	2.28
Xylene (isomer No. 1)	4.47	7.89
Styrene	0.71	0.28
Xylene (isomer No. 2)	1.29	2.52
2-Ethoxyethyl acetate	2.03	1.20
C_3-Benzene (isomer No. 1)[b]	0.47	0.33
C_3-Benzene (isomer No. 2)[b]	0.57	0.35
C_{10}-Alkane (isomer)[c]	0.83	0.76
C_{11}-Alkane (isomer)[d]	0.72	0.60
n-Propyl acetate	1.50	1.00
2-Propanol, 1-(2-methoxy-1-methylethoxy)-isomer No. 1	0.46	0.14
2-Propanol, 1-(2-methoxy-1-methylethoxy)-isomer No. 2	0.49	0.16
2-Cyclohex 4-1-one,trimethyl (isomer)	1.28	0.54

[a] Average of split sample.

[b] Compounds containing three carbons associated with a benzene ring.

[c] Compounds containing ten carbons associated with an alkane.

[d] Compounds containing eleven carbons associated with an alkane.

TABLE III. POHCs IN WASTE FUEL

POHC	Waste fuel concentration, %					Waste fuel mass rate (W_{in}), g/min				
	1	2	3	4	5	1	2	3	4	5
Methyl ethyl ketone	1.99	1.78	1.83	2.81	4.25	332	390	254	328	564
Methyl isobutyl ketone	1.53	1.70	1.41	1.12	3.90	255	373	195	131	518
Tetrachloroethylene	0.19	0.19	0.17	0.06	0.03	31	43	24	7	4
Toluene	8.38	9.27	8.21	7.99	7.54	1,397	2,033	1,137	932	1,000

TABLE IV. WASTE FUEL CONDITIONS

Run number	Chlorine, %	Sulfur, %	PCB, ppm	Heat value, Btu/lb	Ash, %	Specific gravity, g/cc	Feed rate, gal/min	Mass rate, g/min
1	1.08	0.41	ND[a]	12,550	7.74	0.966	4.56	16,670
2	1.08	0.41	10	11,450	7.28	0.922	5.84	21,930
3	1.04	0.39	ND	12,740	7.47	0.978	3.74	13,850
4	0.55	0.26	ND	9,530	15.5	1.07	2.88	11,660
5	0.55	0.42	ND	12,670	6.18	0.966	3.63	13,270

[a] ND - not detected, detection limit = 0.1 ppm.

Table V. DESTRUCTION AND REMOVAL EFFICIENCIES OF POHCs

Run number	DRE, %			
	POHC 1 (MEK)	POHC 2 (MIBK)	POHC 3 (Perc)	POHC 4 (Toluene)
Day 2				
Range	99.999- >99.999	99.999- >99.999	99.999- >99.999	99.999- >99.999
Average	99.999	99.999	99.999	99.999
Day 3				
Range	99.968- 99.999	99.998- 99.999	99.998- 99.999	99.999- 99.999
Average	99.992	99.999	99.999	99.999
Day 4				
Range	99.998- 99.999	99.986- 99.998	99.993- 99.998	99.995- 99.999
Average	99.999	99.995	99.997	99.998
Day 5				
Range	99.999- >99.999	99.999- 99.999	99.991- 99.997	99.998- 99.999
Average	99.999	99.999	99.995	99.999
Overall Average	99.998	99.998	99.997	99.999

relative difference. The overall DRE average for Perc was 99.997% ± 0.004% (95% confidence limits).

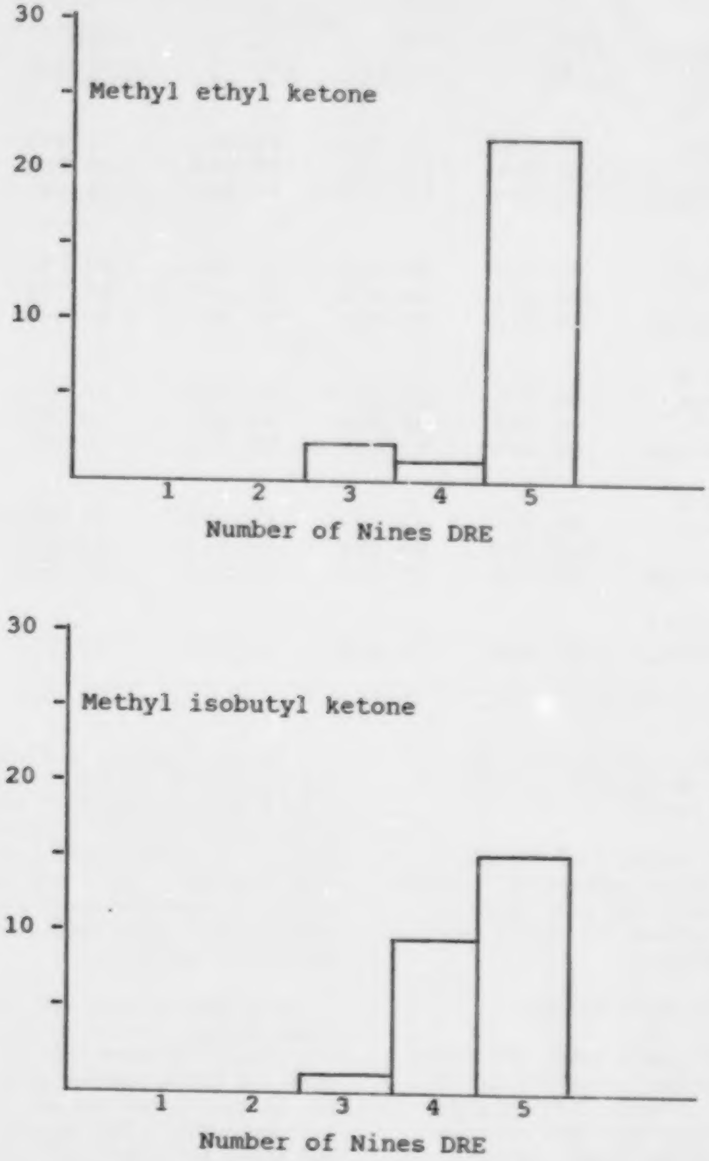
DREs toluene ranged from 99.995% to >99.999%. The overall average for toluene was 99.999% ± 0.002% (95% confidence limits), making toluene the easiest POHC to destroy and remove.

VOST S & A Split Results

Because VOST sample tubes are thermally desorbed, analytical splits for QA/QC purposes are extremely difficult and typically not attempted. This disadvantage of using a conventional thermal desorption technique is that once the sample is desorbed into the analytical system and is expended, there is no way of reanalyzing the sample. Therefore, one cannot run duplicates or adjust for scaling or instrument sensitivity problems if the sample is not in an appropriate concentration for the analytical conditions.

To overcome this analytical deficiency and provide an estimate of VOST precision, a test run was specified in the QA Plan in which two VOSTs were sampled simultaneously through the sample port with the probes tied together. While this was not a true split, it nevertheless represented a whole method (S&A) split rather than only an analytical split.

Only one "within lab" split was specified; however, while in the field, two additional "between lab" split runs were made and these samples were split with the EPA QA contractor who was conducting a systems audit. The "within lab" split at MRC shows excellent duplication and precision for all POHCs except MEK (relative difference = 152%). However, even a difference of 152% for MEK on Runs 3D and 3D' did not affect the final destruction efficiency of 99.999% for each run, as shown in Table VI. VOST samples split between labs (MRC and QA contractor) showed good duplication for all POHCs except MEK. In



(continued)

Figure 2. Destruction and removal effeciencies.

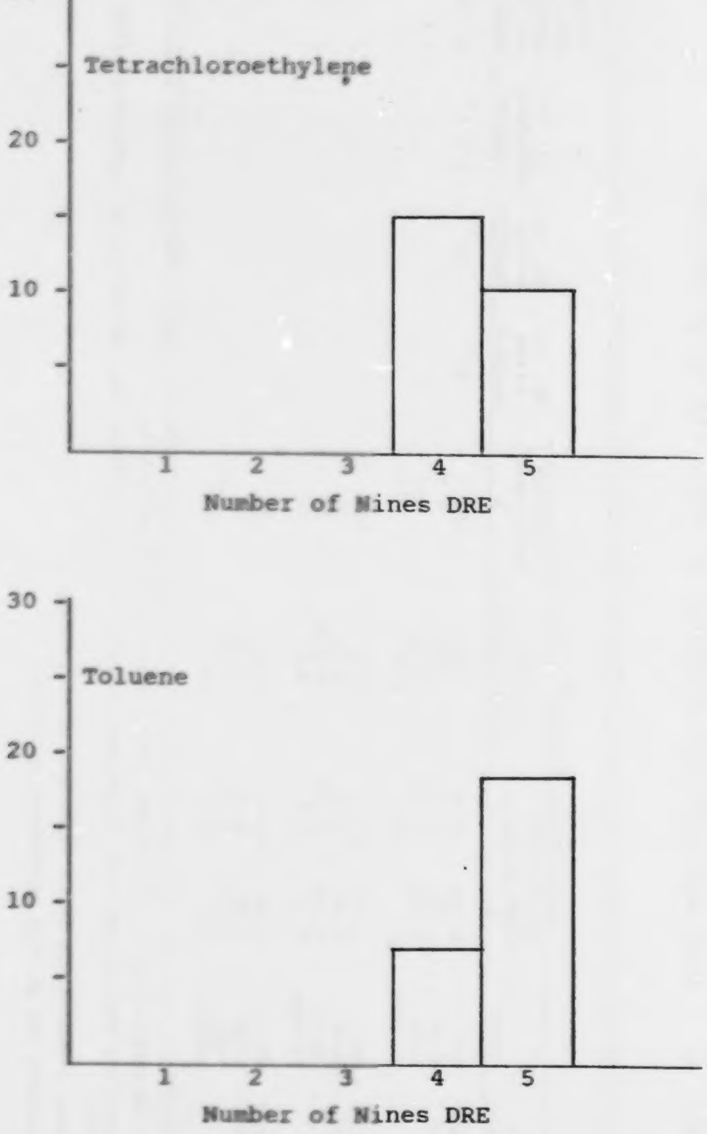


Figure 2 (continued)

TABLE VI. POHC SAMPLING AND ANALYSIS OF STACK GAS QA/QC RESULTS

Number of split samples	Run number	POHC	Split sample results[a] Result Wout, g/min x 10^{-3} 1	2	Average, g/min x 10^{-3}	Relative difference, %	No. of blank samples	No. of spiked samples	No. of standard samples	Completeness goals, % (No. of actual samples taken and analyzed/goals x 100)
1 (within lab)	3D and 3D^{1}	MEK	0.343	2.53	1.44	152	13[b]	43[c]	4 x 5[d]	81 (25/31 prs)
		MIBK	1.90	1.81	1.86	4.9				
		Perc	0.306	0.328	0.317	6.9				
		Toluene	12.3	12.0	12.2	2.5				
2 (between labs)	3A and 3A^{3}	MEK	1.13	37.3	19.2	188				
		MIBK	3.88	2.75	3.32	34				
		Perc	0.508	0.393	0.451	25				
		Toluene	5.39	13.6	9.5	86				
3 (between labs)	3B and 3B^{3}	MEK	2.35	80.4	41.4	188				
		MIBK	1.92	3.38	2.65	55				
		Perc	0.259	0.253	0.256	2.3				
		Toluene	17.1	12.3	14.7	33				

[a] Simultaneous side-by-side sample runs, 1 within MRC lab, 2 split with QA contractor.

[b] Includes two field pairs (one pair to MRC, one to QA contractor), four trip blanks, two lab and three baseline samples for total of 13 samples.

[c] Tube spiked with internal standard, 25 front tubes and 18 back tubes.

[d] Four POHC external standards run at five concentration levels.

this case, the DREs for MEK were affected (i.e., Run 3A DRE = 99.999%, Run $3A^{3}$ DRE = 99.985%). Causes for this difference in MEK results are uncertain but may include contamination of the tubes with MEK and analysis performed by different labs.

Stack Samples

Results for particulate, hydrogen chloride, sulfur dioxide, and nitrogen oxides are summarized in Table VII. Particulate emissions of 5.3 kg/hr (11.7 lbs/hr) were less than air permit regulations for this site issued by the Florida Department of Environmental Regulations (DER) of 8.82 kg/hr (19.43 lb/hr). The first SO_2 test result had a low value of 270 ppm and is considered an outlier when compared to the remaining seven SO_2 test results which ranged 1,030 to 1,470 ppm. The low NO_X value of 40 ppm was expected as it occurred on Day 3 during start-up of the kiln.

Chlorine and Metals Balance

As shown in Table VIII, the amount of chlorine contributed by the waste fuel is 61-85% of the total chlorine to the kiln. The scrubber influent water contributes the remaining 15-39% of the chlorine to the kiln. Virtually all the chlorine leaving the kiln does so in the scrubber effluent.

Table VIII shows material balance for selected metals. The clay feed and waste fuel contribute the largest percentage of metals to the kiln process, while the aggregate product and scrubber effluent filtrate contain the majority of metals leaving the kiln. Difficulties in achieving good material balance closure include the crude estimates for coal usage, clay input, and product output rates (not metered) and the analytical variability inherent in ICP analyses. The goal of determining the major contributers of certain elements and their ultimate fate were met, however.

TABLE VII. AVERAGE RESULTS FOR STACK GAS, PARTICULATES, HCl, SO_2, AND NO_X EMISSIONS

Parameter and unit	Range	Average	Standard deviation
Stack flow rate, m^3/min	623 - 673	652	19
Stack moisture, %	21.5 28.8	26.2	3.3
Stack velocity, m/sec	16.6 - 17.1	16.8	0.2
Particulates			
mg/dscm	163 - 273	215	48
kg/hr	4.4 - 6.5	5.3	1.0
HCl, ppm	0.15 - 0.68	0.46	0.22
SO_2, ppm	270 - 1,470	1,130	380
NO_X, ppm	40 - 227	162	67

CONCLUSIONS

The results of the program were as follows:

Constant achievement of at least 99.99% destruction and removal effeciency was demonstrated for each POHC (MEK, MIBK, Perc, and toluene) in the aggregate kiln process.

Emission of pollutants were determined and ranged as follows: particulates - 4.4 to 6.5 kg/hr; HCl - 0.008 to 0.034 kg/hr; SO_2 - 72.2 to 99.6 kg/hr; NO_X - 1.9 to 11.7 kg/hr.

Approximately 60-90% of the chlorine is fed to the kiln from the waste fuel, while virtually all the chlorine exits the kiln from the scrubber effluent water.

The major percentage of any metal is fed to the kiln from the clay feed and waste fuel, while the major percentage of any metal exits the kiln in the aggregate product and scrubber effluent filtrate.

TABLE VII. CHLORINE MATERIAL BALANCE

Run number	Materials to kiln, % Coal	Waste fuel	Scrubber influent	Clay feed	Total in, lb/hr	Materials from kiln, % Aggregate product	Scrubber effluent	Stack gas	Total out, lb/hr	Material balance closure, %
1	<1	85	15	<1	27.9	<1	99	<1	18.2	65
2	<1	81	19	<1	38.5	<1	100	<1	26.4	69
3	<1	83	17	<1	22.9	<1	100	<1	22.0	96
4	<1	67	33	<1	12.7	<1	99	<1	14.8	117
5	<1	61	39	<1	15.8	<1	99	<1	10.1	64

TABLE VIII. TYPICAL TRACE METAL MATERIAL BALANCE[a]

	Percent to kiln					Percent from kiln					
							Scrubber effluent				
Metal	Coal	Waste fuel	Scrubber influent	Clay feed	Total in, kg/hr	Aggregate product	Liquid	Solid	Stack gas part.	Total out, kg/hr	Percent closure
Al	1	<1	<1	98	362	66	2	32	<1	127	35
Ba	4	43	<1	53	0.92	8	<1	92	<1	2.3	250
Be	3	<1	<1	97	0.019	41	3	56	<1	0.010	53
Ca	2	27	4	67	42	54	18	28	<1	14	33
Cr	1	28	<1	71	1.2	36	1	63	1	0.91	76
Mg	1	1	1	97	47	65	4	31	<1	13	28
Na	4	11	1	84	59	48	3	49	<1	57	97
Ni	<1	7	<1	93	0.24	22	4	70	4	0.17	71
Pb	<1	85	<1	15	2.7	2	1	96	3	8.4	311
Zn	<1	68	<1	32	1.2	13	5	80	2	0.55	46

[a] Values are averages of five runs.

EFFECTS OF DISPOSAL OF HAZARDOUS WASTES IN CEMENT KILNS ON CONVENTIONAL POLLUTANT EMISSIONS

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INTRODUCTION

To turn the old adage around, "one man's poison is another man's meat" has taken on a more literal meaning as the RCRA regulations for hazardous waste incineration have become promulgated [1]. Because many industrial waste products can be readily used as fuels or processed into supplemental fuels, a waste fuel market has been rapidly developing in the U.S. [2]. If reprocessed waste liquids do not contain significant quantities of toxic metals, halogenated materials, or any publically sensitive organics (such as PCBs), they can be economically substituted for coal, coke, oil or natural gas in many industrial processes. The list of high temperature industrial furnaces/processes is larger than one may think, and many of these already burn hazardous waste as supplemental fuel at some facility: cement kilns (both wet and dry process), lime and dolomite kilns, fuller's earth (kitty litter) kilns, steel production blast furnaces, phosphate rock calciners and dryers, iron one dryers, brick and tile tunnel kilns, mineral wool furnaces, and glass melt furnaces.

Cement kilns, in particular, have become the process heater leader in using industrial wastes as supplemental fuel for several reasons: 1) the product (clinker) cost is extremely energy intensive and any fuel cost savings gives an economic/competitive advantage; 2) cement clinker quality is relatively insensitive to addition of trace impurities; 3) cement plants are typically located near population and industrial centers; 4) kiln temperatures and gas residence times are well in excess of that seen in most hazardous waste incinerators; and 5) regulations enacted under Subtitle C of RCRA provided incentives for waste disposal outside of conventional hazardous waste incineration under the aegis of energy recovery.

The Incineration Research Branch of EPA's Industrial Environmental Research Laboratory-Cincinnati has has been researching hazardous waste incineration in industrial furnaces since 1977. A number of test programs on waste incineration at cement plants have been conducted since 1974 in Canada, the U.S., and Western Europe. The tests documented in the available literature include:

1. St. Lawrence Cement Mississauga, Ontario [3,4]
    - waste oil and high chlorinated organic waste with No. 6 fuel oil a dry process kiln equipped with suspension preheaters, air pollution control by ESP.
2. Stora Vika Test Center, Stora Vika, Sweden [5,6]
    - highly chlorinated organic waste, PCBs, and Freon TF with coal in a wet process kiln with ESP.
3. Marquette Cement, Oglesby, Illinois [7]
    - low chlorine (<5%) organic waste with coal in a dry process kiln with ESP.
4. San Juan Cement, Dorado, Puerto Rico [8]
    - highly chlorinated organic waste with Bunker C fuel oil in a wet process kiln with fabric filter.
5. Rockwell Lime, Manitowoc, Wisconsin [9]
    - low chlorine organic waste with coke and natural gas in dry process dolomite kiln with fabric filter.
6. Los Robles Cement, Lebec, California [10]
    - low chlorine organic waste with coal in a dry process kiln with fabric filter.

This paper summarizes the available information on changes in conventional pollutant emissions when burning hazardous wastes. The example test programs have been chosen because testing was conducted during primary fuel firing (baseline) conditions in addition to waste combined with primary fuel firing conditions. This comparison testing allows the tools of statistics to be used to evaluate whether changes in emissions occur.

STATISTICAL TESTING FOR CHANGE

In a variety of situations, decisions must be made concerning whether a new set of test results represents a significant change when compared to the old or typical test results. Sometimes the results of a change may be obvious. In other cases, however, it may appear that a change has occurred, but it is not clear that the change is enough to justify the claims or problems that can accompany such changes. Decision-making becomes more difficult in such a situation, and a decision to endorse or condemn a new process, based on data from small samples, can be difficult.

In the context of this investigation, this means that one wants to know "if the conventional pollutant emissions from a kiln burning hazardous waste as supplemental fuel are truly different from normal emissions." One wants to be confident that the results are correct and spend no more money than is really necessary. Statistical design and interpretation is the only way to meet this objective [11]. A fairly simple procedure called the "one-sided t-test" enables us to decide, to a subjectively selected degree of certainty, whether a statistically significant difference exists between one set of data and another (assuming that the sample populations have approximately normal distributions).

If one takes stack samples from the same stack on two separate occasions and analyzes those samples, the measured concentration will nearly always be different for the two samples. There are probably four principal sources of this variability:

- variability resulting from actual changes in pollutant concentration due to the effect of two different operating conditions (normal and waste firing)

- variability observed and inherent in a large-scale combustion process
- variability introduced as a result of the sampling procedure
- variability in the analytical procedure

To determine whether a change has occurred, one must subtract or otherwise take into account the variability from the process and sampling and analysis, and simply compare the actual concentrations. Proper application of the t-test makes this distinction possible [11].

All that one needs to use the t-test is a computation of the mean and standard deviation of each data set, one-button features on modern scientific hand calculators. In comparing two means, it is not necessary that they be made up of the same number of terms. A mean of 14 measurements made under one test condition can be compared with the mean of 6 measurements made under another test condition. As long as the number of measurements, represented by n_A and n_B, are correctly applied in the equations and the degrees of freedom corresponding to $n_A + n_B - 2$ are used, the resulting t-test will be applicable.

The t-value is calculated using the following equation:

$$t = \frac{|X_A - X_B|}{\left[\frac{s^2A}{n_B} + \frac{s^2B}{n_B}\right]^{\frac{1}{2}}}$$

where X_A and X_B = two separate means
n_A and n_B = number of values from which X_A and X_B are, respectively, the means
s_A and s_B = standard deviations of each data set

This calculated t-value is compared to a tabulated value of t at a known probability level, usually 5% or 1% (equivalent to a 95% or 99% confidence level). When the calculated t-value is less than the critical tabulated t-value, we say there is no significant difference between the means. What we are really saying is that with the observed variation of the measurements involved we cannot tell whether the observed difference between the means is due to some real cause or is due to fluctuations in the measurements. If t-calculated is greater than t-tabulated, then mean X_A is significantly different than mean X_B.

One must always remember that statistical tests are based on probability, consequently there is some chance that the wrong conclusion is reached. The choice of the probability level defines the degree of chance that the wrong conclusion was reached. For instance, the use of 0.05 probability level (95% confidence level) means that the conclusion reached from using the t-test has a 5% chance, or 1 in 20, that it is incorrect. Conversely, you could give odds of 20 to 1 that the correct conclusion was reached.

PARTICULATE MATTER

An excellent review and discussion of the formation of particulate emissions when chlorinated wastes are added as fuel to a cement kiln is provided by Weitzman [12]. Data from the St. Lawrence Cement and Stora Vika tests were re-examined, compared, and plotted as a function of chlorine feed rate with respect to clinker production rate, which clearly demonstrate a linear increase in particulate emissions as a function of chlorine input. The hydrogen chloride combustion product reacts with the potassium, sodium, and calcium compounds in the hot kiln to form the respective chlorides. These volatized chloride salts are carried by the hot gas to the cold end of the kiln where they condense at about 800-900°C to form a fine particulate. The character of this new particulate and resultant change in dust resistivity lowered the electrostatic precipitator (ESP) collection efficiency and produced significantly increased dust emissions during these two chlorinated organic waste firing tests. Based on his presumption of formation of very fine particles, he prognosticated that a kiln using a fabric filter rather than an ESP for particulate control would encounter similar changes in efficiency.

Two other tests conducted at kilns equipped with an ESP--waste oil at St. Lawrence Cement and low chlorine (<5%) waste at Marquette Cement--did not demonstrate an increase in particulate emissions. Comparison between baseline and waste firing at Marquette Cement showed no statistically significant difference, an expected result when one examines the linear relationship between chlorine input and particulate emissions. A statistically significant difference was seen, however, for the nonchlorinated waste oil experiments at St. Lawrence Cement--a decrease in particulate emissions. This improvement was attributed to the additional water introduced (in the waste oil), which been shown to improve cement kiln ESP efficiency even at gas temperatures of 350°C [3].

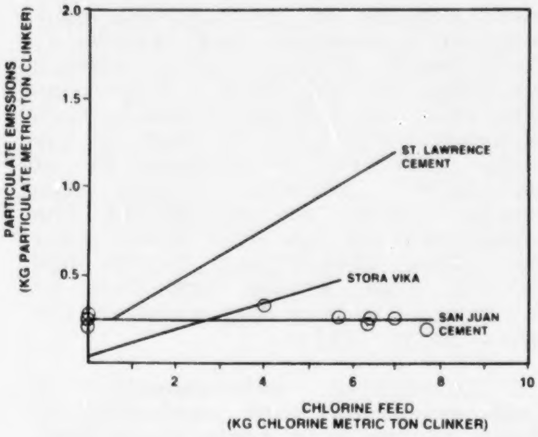

Figure 1. Variation of particulate emissions with chlorine feed at the three high chlorine feed to kiln tests.

The particulate emissions from the kiln tested at San Juan Cement, equipped with a fabric filter dust collection system, did not exhibit an increase with progressively larger chlorine input as shown in Figure 1. The linear regression curves from the St. Lawrence Cement and Stora Vika tests are also displayed for comparison. It can be seen that, not only was more organic chlorine fed to the kiln at San Juan Cement than the previous highly chlorinated waste tests, the fabric filter system was able to maintain a high collection efficiency regardless of the changed character of dust from the kiln. An ancillary part of the San Juan Cement test program was Extraction Procedure (EP) Toxicity tests on the baghouse dust collected during waste firing. Also, the same dust was extracted and analyzed for polychlorinated dibenzodioxin and furan isomeric groups. None of the compounds tested for were found in these analyses and the baghouse dust EP Toxicity tests results matched the landfill suitability results obtained in a much larger survey of cement kiln dusts [13].

Thus, the addition of substantial amounts (>5%) of organic chlorine in waste fuel is the "bad actor" in lowering ESP collection efficiency, but no drop in control effiof fabric filters will result. An ESP vendor could "fine-tune" the ESP to overcome the change in dust resistivity as long as the ESP is well maintained.

Noteworthy in all the tests described above was that particulate concentrations were well below the RCRA performance standard of 180 mg/m^3 for a hazardous waste incinerator.

PARTICULATE LEAD

The choicest waste streams for waste fuel use in kilns are generated by paint, ink, and coating users because of the high Btu content of solvents and alcohols. These waste fuels usually contain suspended solids, with a high concentration of inorganic metals such as lead. The fate of lead in the waste incineration process is of particular interest because the health effects are recognized, the concentrations in the waste fuel are often significant (>1000 ppm Pb),and implications are that it may become widely dispersed in the environment [14].

Comparison measurements of lead emissions were conducted at three of the kiln tests described: St. Lawrence Cement in 1974 burning a waste oil contaminated with 6,000 ppm (0.6 wt. %) lead; Marquette Cement burning waste solvents contaminated with 1,050 to 2,520 ppm lead; and Rockwell Lime burning waste solvents contaminated with 128 to 139 ppm lead. These three tests provide distinctly different rates (almost order-of-magnitude) of lead input to a kiln.

Lead emissions at Rockwell Lime increased slightly with waste firing to 1.7 g/hr, and a statistically significant difference was noted at the 95% confidence level. The measured emission rate of 1.7 ± 0.25 g/hr (standard deviation included) is equivalent to an automobile driven at 30 mph using leaded fuel. An automobile traveling at 60 mph will emit 3.54 g/hr and also re-entrain 1.9 g/hr of fugitive lead dust from a paved highway [15].

At Marquette Cement the addition of waste firing reduced lead emissions by almost one-half, but this was not a statistically significant difference. Apparently, the substitution of waste fuel for coal caused the reduction in lead emitted. The lead emissions while burning waste fuel contaminated with 1,050 to 2,520 ppm lead is equivalent to emissions from ten automobiles traveling 30 mph (neglecting re-entrained dust contributions).

A similar reduction in lead emissions of almost one-half was measured at St. Lawrence Cement when contaminated waste oil was burned. Because more tests were run and better precision was obtained with-in each data set condition, a statistically significant difference was noted for these data. Again, large energy substitution for coal may have caused the lead emission reduction. The waste oil firing emission rate of lead was equivalent to three automobiles traveling at 30 mph.

CARBON MONOXIDE

As part of the regulatory requirements under RCRA, carbon monoxide is continuously monitored in the exhaust gas of hazardous waste incinerators as an indicator of combustion efficiency (not as a surrogate compound for DRE's). Moreover, the waste feed cutoff system is coupled to a maximum CO level specified in each incinerator's Part B permit, established from Trial Burn results.

The term "combustion efficiency" is used as a measure of a combustion unit's performance. Conceptually, this term defines the percentage of emissions that are completely oxidized to CO_2, and is mathematically defined as:

$$\% \text{ CE} = \frac{CO_2}{CO_2 + CO} \times 100$$

where CO_2 and CO are expressed in ppm by volume. More rigorous definitions of combustion efficiency can also include denominator values for THC (expressed in ppm volume as methane) and Cp (expressed in ppm volume assuming smoke particulate as gaseous elemental carbon and ideal gas, 2.03 L/g).

Cement production is a calcination process in which large amounts of CO_2 are liberated from the feed to the exhaust gas. In fact, the CO_2 from calcination is more than double the CO_2 from combustion and confounds a combustion efficiency determination.

CO concentrations in cement kilns can range from 10 ppm up to occasional excursions in the percentage range; a smooth kiln operation is typically indicated by CO concentrations of 50 ppm or less. Our observations of CO from kilns have convinced us that any process change creates significant CO excursions, independent of waste firing. Some examples which temporairly increase CO concentrations are changes in the primary air/fuel ratio, any change in clinker cooler air (secondary air), irregular solid fuel feed rates, and changes in exhaust damper setting. These CO "spikes" are indistinguishable from the increased CO observed for waste fuel introduction and shutoff at San Juan Cement [16]. Thus, CO is more an indicator of process stability in calcination kilns than combustion efficiency.

At two other kiln tests--Los Robles Cement and Rockwell Lime--where CO was monitored continuously, seemingly different results were observed. CO concentrations at Rockwell Lime fluctuated often during both baseline and waste firing periods such that the mean concentrations were similar and the standard deviations large. Naturally, the t-test conclusion was that no significant difference exists.

On the other hand, the Los Robles Cement kiln demonstrated excellent process stability, i.e. low CO concentrations. During three waste firing test periods the maximum CO concentration was 100 ppm, a value which is easily exceeded due to any process change. An earlier series of baseline tests has a CO maximum of 618 ppm with daily average CO concentrations 2-6 times higher than daily averages during waste firing. Although the raw data were not available for statistical testing, the very narrow ranges of CO concentrations reported during waste firing suggest that a t-test would show that a significant difference lower. This would be a misleading use of a statistical tool given the experiences described above.

TOTAL HYDROCARBONS

Total hydrocarbon analyzers using a flame ionization detector have been proposed as possible regulatory tool for testing and online evaluation of incinerator performance [17]. The evaluation method for hazardous waste incineration involves determining the total unburned hydrocarbons in the combustion gases and calculating the overall destruction of the hydrocarbons in the feed. The theory is that an incinerator producing significant amounts of unburned hydrocarbons is not approaching thermodynamic equilibrium and will not pass the overall performance test of 99.99% DRE of individual compounds.

This proposed monitoring tool may be workable for incinerators and even boilers which burn waste fuels, but testing experience has shown that kilns do not exhibit enough change in total hydrocarbon (THC) emissions. The main reason is that the primary fuel still comprises 60% or greater of the energy input to the kiln. Unburned carbons, THC emissions, have a baseline level which exists for this fuel, typically from 4 to 8 ppm THC (quantified as methane). The addition of a secondary waste fuel simply does not cause enough change in THC emissions, which, measured continuously, exhibit very smooth concentration curves and no wide fluctuations. A kiln process change which causes a CO spike goes unnoticed on the THC analyzer.

Results from the Stora Vika tests show that THC concentrations were less than 10 ppm for baseline, chlorinated aliphatics fired, and Freon TF fired, but rose to 10 ppm when chlorinated aromatics were burned. The data were not in a form amenable to statistical analysis. At San Juan Cement a statistically significant difference (and increase) was observed when chlorinated aliphatics were burned to partially offset fuel oil, presumably because the addition of high levels of chlorine made complete combustion more difficult. At Rockwell Lime and Marquette Cement, however, a significant difference (and decrease) was observed. At both of these tests, a low chlorine waste fuel was burned at high energy substitution to offset solid fuel and complete combustion was probably enhanced.

NITROGEN OXIDES

Nitrogen oxides are formed by the oxidation of nitrogen (N_2) in air or nitrogen compounds in fuel. Because nitrogen has oxidation numbers ranging from -3 to +5, it is possible to form many different oxides. Nitrogen oxides (NOx) consist mainly of NO and NO_2, with a typical ratio of NO_2 to NO of 2:1. Most current sampling and analytical techniques rely on oxidation of NO to NO_2, and report concentrations as NOx.

In industrial kilns there is a direct functional relationship between NOx emissions and secondary air, which is heated air from the product cooler. There is usually little to no NOx formed from nitrogen in fuel relative to NOx from combustion air. Kilns are generally operated as "poor" combustors when compared to boilers; they have a reduced primary air/fuel mix, poor secondary air mixing, and often require a confined, narrow flame configuration for product quality. Typical NOx concentrations in the flue gas can range from 200 to 1500 ppm, even within hours at the same kiln. NOx levels are very operator-dependent; continuous monitoring has shown that at some kilns NOx levels vary widely from hour to hour, and others can maintain steady NOx concentrations. The absence or addition of waste firing has little to do with NOx variations. The effect of excess air and its temperature are the main determinants in kiln NOx emissions.

At both Marquette Cement and San Juan Cement a significant difference (decrease) was observed with the addition of waste firing. This may have been the result of lowered oxygen input more than addition of waste firing. At Los Robles Cement the NOx emissions decreased slightly but it was not statistically significant. A significant increase was observed at Rockwell Line, but this was due to operator intent to increase the NOx emissions during waste firing.

A definite relationship between O_2, NOx, and SO_2 in calcination kilns has been shown [18]. NOx emissions increase with increasing O_2 input and degree of preheating, while SO_2 emissions decrease. For instance, a 38% reduction in NOx due to O_2 lowering can cause a 47% increase in SO_2. Continuous monitoring at Rockwell Lime illustrated that NOx and SO_2 change simultaneously, as shown in Figure 2. Moreover, the NOx/SO_2 change is followed within 5-15 minutes by a CO spike, the kiln's indicator of a momentary process instability. As shown in Figure 2, this event was recurring.

ACID GASES

Cement kilns are, by their alkaline nature, built-in control devices for acid gases such as SO_2 and HCl. In a well operated cement kiln with medium-to-high feed alkalinity, SO_2 will be absorbed

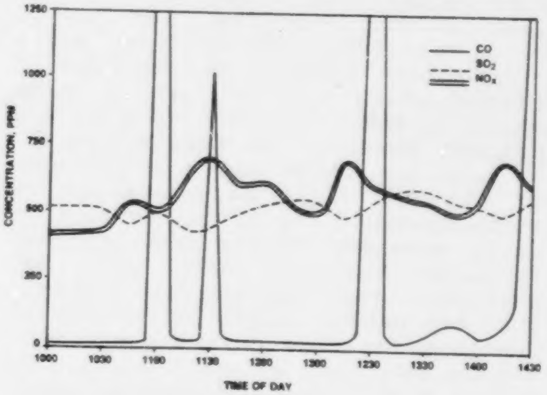

Figure 2. Illustration of interrelationship between NOx, SO_2, and CO emissions in a lime kiln.

(scrubbed) in the kiln environment and alkaline dust of the APCD to control efficiencies of greater than 90%. For HCl emissions a removal of efficiency greater than 99% was observed at San Juan Cement, where high chlorine levels were added to a relatively low alkaline kiln.

Waste fuels typically do not contain much sulfur and thus the partial substitution of waste fuel for fuel oil or coal will reduce sulfur input to the kiln. This will result in even less theoretical SO_2 to be formed. At Marquette Cement, where a 13% energy substitution was fired, SO_2 stack gas concentrations were reduced from 93 ppm to 18 ppm. At Los Robles Cement no significant difference in SO_2 emissions was noted. SO_2 emissions increased significantly at San Juan Cement, from 280 ppm to 450 ppm, probably for two reasons: the NOx emissions were reduced--indicative of lower O_2 input--and the high rate of chlorine input may have caused a competitive acid gas "scrubbing" situation--HCl was preferentially absorbed over SO_2. The kiln operator's choice of O_2 input will have a greater effect on SO_2 emissions than addition of a waste fuel. It is possible to operate a cement kiln with less than 50 ppm SO_2 in the stack gas.

At Rockwell Lime, however, a different mode of operation was required; SO_2 emissions are intentionally not absorbed because the presence of sulfur in lime is undesirable. No significant difference was observed for SO_2 emissions, which remained between 500-600 ppm regardless of waste firing.

CONCLUSIONS

The foregoing technical examples of burning liquid hazardous wastes as a fuel supplement in cement and lime kilns in Canada, Sweden, Illinois, Puerto Rico, California, and Wisconsin have demonstrated that, often times, emissions of conventional pollutants are reduced and that process operation changes have a greater effect on changes in emissions than the partial substitution of waste as fuel. It is a tribute to the expertise of the operators at each plant tested that they were able to make product while burning a new and different fuel mix. A new hazardous waste incinerator is permitted 720 hours of "shakedown" operation before a trial burn is conducted; these test situations were not allowed that luxury and the operator's skill in burning waste fuels could only improve with practice.

Before kilns are allowed to routinely burn hazardous waste liquids, monitoring devices capable of assuring the environmental adequacy of the burning operation should be identified. The amount of information now available concerning process variables is insufficient to identify a single adequate monitoring system. Equipment capable of detecting trace amounts of unburned hydrocarbons have been shown to be inappropriate because of the predominance of unburned hydrocarbons from the primary fuel. The emission tests which have included continuous monitoring for SO_2, NOx, O_2, and CO have demonstrated that combustion operation can be (with training) easily optimized. Addition of these monitors is an excellent operating tool because of the increased feedback and decreased response lag times compared to air flow, temperator, and undergrate pressure sensors, but such continuous monitoring (and subsequent reporting) is excessive as a regulatory tool. They require constant attention, calibration, and maintenance. Unfortunately, the combination of monitors is valuable and no single monitor serves the purpose.

Further research should be conducted to identify the simplest monitoring techniques that can be used to effectively ensure the safety of waste firing. The identification of adequate monitoring systems entails a thorough understanding of the mechanism by which waste destruction occurs in kilns.

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EVALUATION OF HAZARDOUS WASTE INCINERATION IN A LIME KILN

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ABSTRACT

During a one-week test burn, hazardous waste was used as supplemental fuel and co-fired with petroleum coke in a lime kiln in eastern Wisconsin. Detailed sampling and analysis was conducted on the stack gas for principal organic hazardous constituents (POHCs), particulates, particulate metals, HCl, SO_2, NO_x, CO, and THC and on process streams for metals and chlorine. POHCs were also analyzed in the waste fuel. Sampling was conducted during three baseline and five waste fuel test burn days. The program objectives were to determine the destruction and removal efficiency (DRE) for each POHC, determine concentration of stack gas pollutants under baseline and waste fuel test burn conditions, determine the fate of chlorine, sulfur, and trace metals in the kiln process, and evaluate kiln performance when operating with hazardous waste as supplemental fuel.

Results show average DRE's greater than 99.99% for each POHC and little change in pollutant emissions from baseline to waste fuel test conditions. In addition, material balance results show that 95% of chlorine enters the process from the limestone feed and the chlorine exits the kiln in the baghouse dust and lime product at 61% and 38%, respectively.

INTRODUCTION

Cofiring of hazardous wastes in high temperature industrial processes is an attractive alternative to hazardous waste incineration. The alternative makes use of the waste's heat content and provides temperatures and residence times similar to those required for incinerators dedicated to incineration of hazardous wastes. In addition to the savings derived from the heat value, the use of existing industrial equipment does not require the capital required if a separate incinerator to process a given amount of hazardous waste is to be built, and it may provide an environmentally acceptable alternative to conventional hazardous waste disposal.

Lime kilns, because of their high enengy use, are an excellent example of this concept. Such kilns typically operate at temperatures over 1093°C (2000°F), have gas residence times in excess of 1.5 seconds, and have a highly turbulent combustion zone. However, the need exists for data that shows the effect of cofiring hazardous waste on the emissions from the lime process.

The State of Wisconsin Department of Natural Resources (DNR) and EPA Region V, in implementing RCRA regulations, issued a temporary permit to Rockwell Lime Company to conduct a hazardous waste test burn. This test would allow the burning of hazardous liquid waste as supplemental fuel along with petroleum coke. The waste fuel would replace natural gas as a fuel component.

Monsanto Company (MC) was contracted by the U.S. Environmental Protection Agency, Office of Research and Development (ORD-IERL) in Cincinnati, Ohio to perform sampling and analysis of stack gases and process samples during the test burn conducted at the Rockwell Lime Company in Rockwood, Wisconsin on April 15 and April 29 through May 6, 1983 under baseline (no waste fuel burned) and waste fuel conditions (coke and waste fuel burned).

The primary objectives of the sampling and analytical program were to (1) determine the effects of cofiring petroleum coke and hazardous waste on the emissions from the kiln, (2) determine the fate of the principal organic hazardous constituents (POHCs) and determine destruction and removal effeciencies (DRE), (3) determine the fate of chlorine and trace metals in the kiln process, (4) determine the concentration of SO_2, NO_x, particulates, HCl, metals, total hydrocarbons, and carbon monoxide in the stack gas at baseline and waste fuel test burn conditions, and (5) evaluate kiln operation during hazardous waste fuel burning condition. This testing would provide to the Wisconsin DNR and the EPA Region V the data necessary to determine whether a permit can be issued to Rockewll Lime Company to burn hazardous waste. The testing also will provide the EPA-ORD with additional data in their research on the incineration of hazardous waste and the environmental problems associated with incineration.

FACILITY AND PROCESS DESCRIPTION

The Rockwell Lime Company operates a lime kiln in Rockwood, Wisconsin, which is located approximately 10 miles north of Manitowac in eastern Wisconsin. Production of lime, which is converted into various forms such as hydrated and barn lime, is approximately 1.3×10^6 kg (1,430 tons) per week, which varies based upon product demand.

The industrial process involves the heating of limestone to a temperature of approximatly 1,093°C (2,000°F) in a horizontal rotary kiln to prepare the lime product. The calcining is achieved by interfacing the hot gases with the limestone which drives off the CO_2 from the limestone, leaving the lime product (CaO).

The kiln, with refractory linings, is 2.4 m (8 ft) in diameter and 67.1 m (220 ft) long. The kiln rotates slowly (approximately one revolution per minute) and has a gentle slope (6 cm/m of length) to allow material to pass through by gravity. The kiln also has a countercurrent flow pattern, i.e., solid materials travel in one direction and hot gases and dust emissions travel in the opposite direction as shown in Figure 1. The coke and natural gas provide a heat input of approximately 14,700 kw (50 million Btu/hr) or approximately 6.5 million Btu/ton of lime product. As the limestone feed travels down the inclined rotating kiln, it passes through various temperature zones, and the hot gases calcine the limestone into the lime product. The product is produced at a rate of approximately 7,720 kg/hr (17,000 lb/hr).

After heating and transformation in the kiln, the lime product is cooled by air and either stored in silos or hydrated prior to storage in silos where it is held until sold.

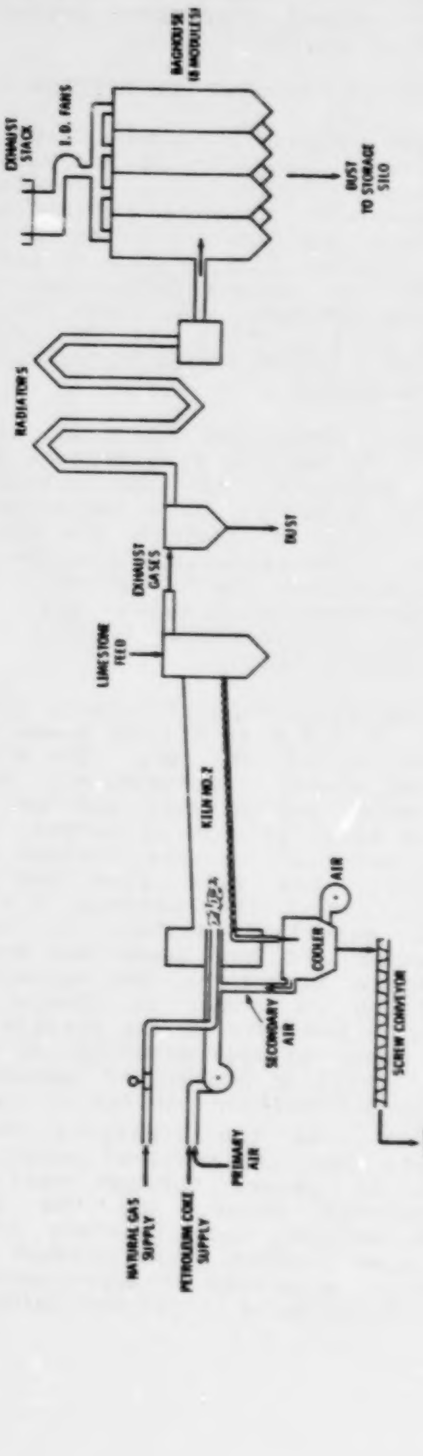
NATURAL GAS SUPPLY
PETROLEUM COKE SUPPLY
PRIMARY AIR
SECONDARY AIR
SCREW CONVEYOR
LIME PRODUCT
COOLER
AIR
KILN NO. 2
LIMESTONE FEED
EXHAUST GASES
DUST
RADIATORS
DUST TO STORAGE SILO
BAGHOUSE (4 MODULES)
I.D. FANS
EXHAUST STACK

Figure 1. Schematic diagram of lime kiln process.

The kiln is fed by primary air mixed with the gas and coke and secondary (heated) air from the lime product cooler, which provides oxygen for the combustion of the coke and natural gas (or waste fuel). The kiln exhaust gases pass through a series of large radiator coolers to cool the gases prior to their entering the baghouse, which removes particulates and SO_2 from the gas stream. The gases then pass through the induced draft fans and out the stack at approximately 200°C (392°F) and 5.5 m/s (18 ft/s). The collected dust is stored in a silo and mixed with water to granulate. Some of the dust is sold and the remainder is disposed of in the quarry. No dust is re-injected into the kiln.

During baseline conditions, a blended combination of petroleum coke and natural gas was used to fire the kiln. During the waste fuel runs, a temporary 1-inch diameter stainless steel pipe was placed on the burner pipe and its nozzle pointed into the flame and the waste fuel and petroleum coke were fed unblended to fire the kiln.

The hazardous waste fuel was temporarily stored in a 5,000-gallon tanker during the test burn. Additional chlorinated organics (tetrachloroethylene and trichloroethylene) were spiked to the waste fuel prior to the test to bring the total chlorine content to approximately 3.0%, which would allow easier evaluation of the destruction of the chlorinated species in the waste fuel.

EXPERIMENTAL PROGRAM

Table 1 summarizes the overall test program and lists each sampling and analytical method used. Sampling was conducted under baseline conditions (i.e., no waste fuel burned) on April 15, 29, and 30. Sampling at waste fuel conditions (i.e., waste fuel burned) was conducted from May 2 to May 6. A Quality Assurance Project Plan was reviewed and approved prior to the test program.

TABLE 1. SUMMARY OF ROCKWELL LIME KILN SAMPLING AND ANALYTICAL PROGRAM

Parameter	Sampling method	Analytical method
STACK GAS		
1. POHCs[a]	Volatile organic sampling train (VOST)	GC/MS, thermal desorption and SIM
2. Particulate matter	EPA Method 5	EPA Method 5
Metals on particulate	EPA Method 5	ICP
3. Hydrogen chloride	Impinger absorption in 0.5 M NaoAc (back half of EPA Method 5)	Specific ion electrode
4. Carbon dioxide and oxygen	EPA Method 3	Fyrite
5. Nitrogen oxides	Continuous	Chemiluminescence photometric analyzer
6. Sulfur dioxide	Continuous	Pulsed fluorescence TECO analyzer
7. Carbon monoxide	Continuous	Infrared-EPA Method 10
8. Total hydrocarbons	Continuous	Flame ionization detector
9. Oxygen	Continuous	Teledyne's micro-fuel cell
10. Waste fuel		
POHCs	Grab → composite	GC/MS
Metals	Grab → composite	ICP
Chlorine, sulfur	Grab → composite	ASTM D240-64
Btu content	Grab → composite	ASTM D482-IP4
11. Baghouse dust		
Metals	Grab → composite	ICP
Chlorine, sulfur	Grab → composite	XRF
12. Lime product		
Metals	Grab → composite	ICP
Chlorine, sulfur	Grab → composite	XRF
13. Dry limestone feed		
Metals	Grab → composite	ICP
Chlorine	Grab → composite	XRF
14. Primary fuel coke		
Metals	Grab → composite	ICP
Chlorine, sulfur	Grab → composite	XRF
Btu content	Grab → composite	ASTM D240-64

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[a] Tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, methyl ethyl ketone, and toluene.

RESULTS AND DISCUSSION

Waste Fuel

A summary of the waste fuel composition for two samples is shown in Table 2. Tables 3 and 4 show the concentration of each POHC and other properties averaged for the five waste fuel samples (one sample per day, Runs 4-8).

POHC Destruction and Removal Effeciencies

The complex combustion chemistry for organic materials becomes perplexing when a broad range of organic compounds present in a liquid waste are burned. On a weight basis, most of the organic carbon in the waste is oxidized to CO_2 in the combustion process, but trace amounts of organic chemicals survive the oxidation process and are only partially reacted. Accordingly, the test burn investigated the amount of destruction of the organic compounds in the hazardous waste.

Destruction and removal efficiency (DRE) for an incineration/air pollution control system is defined by the following equation:

$$DRE = \frac{W_{in} - W_{out}}{W_{in}} (100) \qquad (1)$$

where DRE = destruction and removal efficiency, %

W_{in} = mass feed rate of principal organic hazardous constituent(s) (POHCs) fed to the incinerator

W_{out} = mass emission rate of principal organic hazardous constituent(s) (POHCs) to the atmosphere (as measured in stack prior to discharge).

DRE calculations are based on combined efficiencies of the destruction of the POHC in the incinerator, or the lime kiln, and the removal of the POHC from the gas stream in the air pollution control system. The presence of POHCs in solid discharges from the air pollution control devices is not accounted for in the DRE calculation as currently defined by the EPA. RCRA Part 264, Subpart O regulations for hazardous waste incinerators require a DRE of 99.99% for all principal organic hazardous constituents of a waste during trial burns unless it can be demonstrated that a higher or lower DRE is more appropriate based on human health criteria. Specification of the POHCs in a waste is subject to best engineering judgment, considering the toxicity, thermal stability, and quantity of each organic waste constituent.

Approximately six VOST sampling runs were made each day (Runs 1-8). Destruction and removal efficiencies, calculated for waste fuel runs 4-8, are summarized in Figure 2. In general, DREs ranged from 99.60% to >99.999% for all compounds and averaged 99.9989%. Only four runs had DREs less than 99.99%; three of these were for methylene chloride, the fourth for 1,1,1,-trichloroethane.

DREs for methylene chloride ranged from 99.60% to <99.999% and averaged 99.983%. Three runs at a DRE less than 99.99% (Run Nos. 5A, 5F, and 4E). In Run No. 5A, the tube mass collected was 1,066 ng compared to a maximum of 55 ng for all of the other runs. This high mass was most likely caused by lab contamination. Run No. 5A is not included in the averages, due to the lab contamination, thus the Day 5 average is 99.995% and the overall methylene chloride DRE average is 99.997%.

Methyl ethyl ketone had an average DRE of 99.999% and ranged from 99.998% to greater than 99.999%. These high destruction efficiencies were consistent throughout the waste fuel test runs.

DREs for 1,1,1-trichloroethane

TABLE 2. RESULTS OF CAPILLARY GC/MS ANALYSIS OF MAJOR COMPONENTS OF WASTE FUELS

Waste fuel component	Concentration, wt % Number 4[a]	Concentration, wt % Number 7[a]
Acetone	0.23	0.22
Methyl ethyl ketone (POHC)	2.48	3.17
1,1,1-Trichloroethane (POHC)	0.24	0.22
1-Butanol	0.32	0.37
Trichloroethylene (POHC)	1.73	2.16
2-Ethoxyethanol	0.85	0.92
Methyl isobutyl ketone	1.06	1.16
Toluene (POHC)	11.0	12.5
Tetrachloroethylene (POHC)	2.17	2.49
Butyl acetone	0.27	0.32
Ethylbenzene	1.42	1.58
Xylene (isomer No. 1)	4.92	5.58
Xylene (isomer No. 2)	1.43	1.60
2-Butoxyethyanol	1.99	2.07
2-Ethoxyethyl acetate	5.91	6.37
C_3-Benzene (isomer No. 1)	0.28	0.32
C_3-Benzene (isomer No. 2)	0.46	0.57
C_{10}-Alkane	0.80	0.94
Alkane $>C_8$	0.24	0.28
Alkane	0.14	0.18
C_{11}-Alkane	1.26	1.48
2-Cyclohexen-1-one	0.15	0.18
Alkane $>C_6$	0.27	0.24

[a] Average of split sample.

TABLE 3. CONCENTRATION OF POHCs

POHC	Average concentration, wt %
$MeCl_2$	0.11
MEK	2.69
CH_3CCl_3	0.24
TCE	1.84
Perc	2.26
Toluene	11.6

TABLE 4. WASTE FUEL CONDITIONS

Parameter	Average concentration
Chlorine, % vol	3.1
Sulfur, %	0.07
PCB, ppm	<1.0
Heat value, Btu/lb	12,870
Specific gravity, g/cc	1.01
Feed rate, gpm Run 4	0.64
5	1.21
6	2.05
7A	0.78
7B	2.90
8	2.88

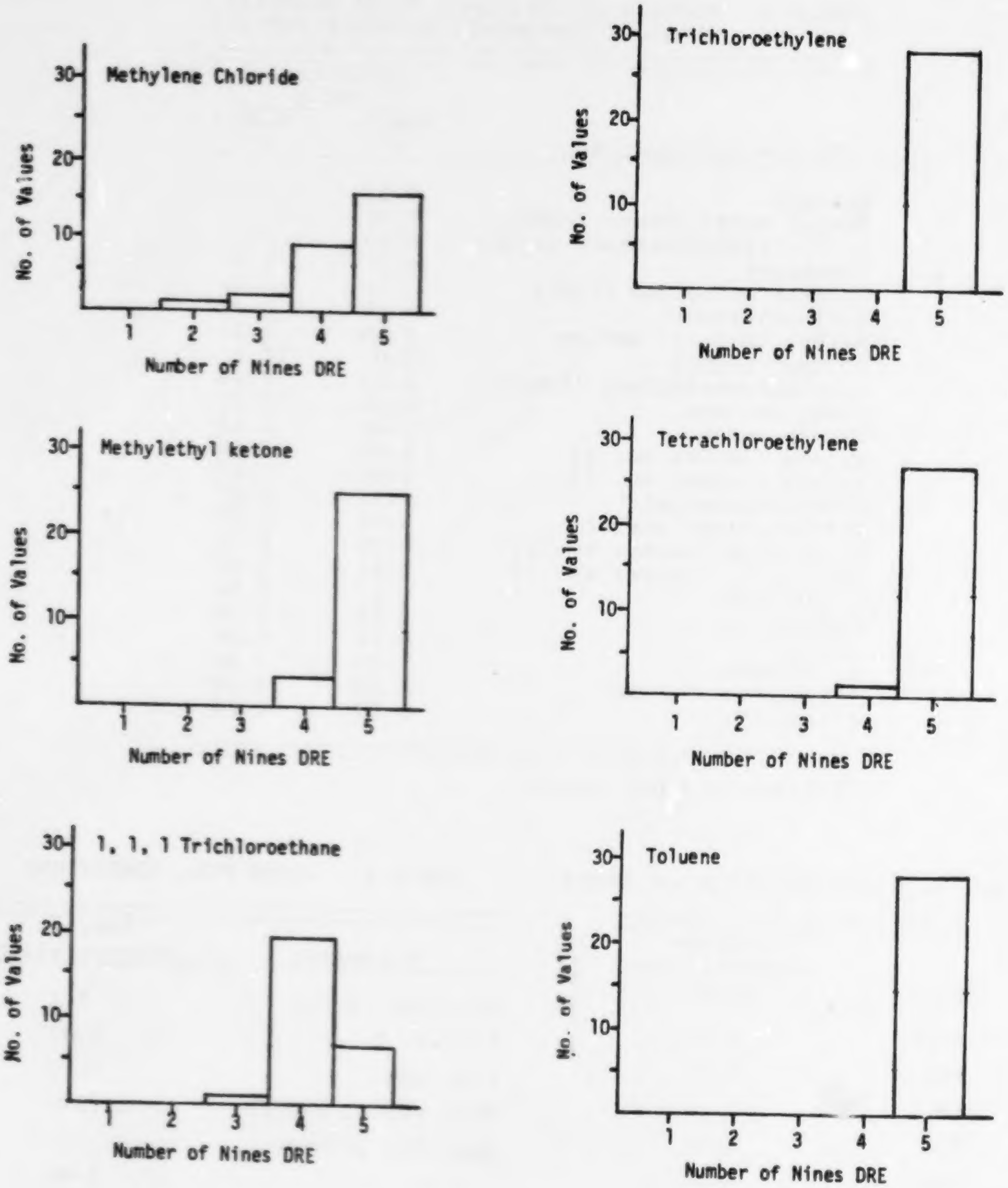

Figure 2. Destruction and removal efficiencies.

ranged from 99.989% to 99.999% and averaged 99.997%. Only Run No. 4E had a DRE less than 99.99%.

DREs for trichloroethylene (TCE) were greater than 99.999% for all runs. TCE was spiked to the waste fuel prior to the waste fuel testing to increase its concentration and allow easier detection of TCE in the stack gas.

DREs for tetrachloroethylene (Perc) also were greater than 99.999% for all runs. Like TCE, Perc was spiked to the waste fuel to the maximum allowable concentration described in the test burn permit prior to the test.

Toluene was the POHC of highest concentration in the waste fuel (average 11.6% by weight). DREs for toluene were above 99.999% for all runs. Data for toluene was very consistent during all waste fuel test runs.

Stack Samples

Results for stack conditions and particulate, HCl, SO_2, NO_x, CO, and THC emissions for baseline and waste fuel runs are summarized in Table 5. The dry stack rate averaged 487 dscm/min (17,210 dscf/min). As evidenced by the high standard deviations the CO and, to a lesser degree, the SO_2 fluctuated. Minor kiln upsets (i.e., coke feed chute cleaning, clumps of coke falling to kiln, change in process conditions) created high CO excurtions. A trend which occurred quite often was an increase in SO_2 by ~200 ppm, followed by a reduction in NO_x by ~50 ppm, following by an increase in CO by ~500 ppm over a 15 minute period. These trends are expected when a lower intensity flame occurs (or kiln upset). However, as revealed by Figure 2, the kiln upsets had little or no effect on the DRE results.

Chlorine, Sulfur and Metals Balance

Chlorine and sulfur material balances are summarized for baseline and waste fuel conditions in Table 6. The majority of chlorine (for either baseline or waste fuel conditions) enters the kiln in the limestone feed and exits the kiln in the lime product and baghouse dust. Sulfur (for either baseline or waste fuel conditions) enters the kiln in the petroleum coke and

TABLE 5. AVERAGE STACK EMISSIONS

	Baseline			Waste fuel		
Parameter and unit	Range	Average	Standard deviation	Range	Average	Standard deviation
Stack rate, m^3/min	805 - 975	917	76	791 - 938	847	52
Stack velocity, m/sec	5.0 - 6.0	5.7	0.4	4.9 - 5.8	5.2	0.3
Particulates						
mg/dscm	24.0 - 35.0	28.7	4.7	24.9 - 48.7	35.3	8.0
kg/hr	0.66 - 1.1	0.9	0.2	0.68 - 1.4	1.0	0.3
HCl, ppm	0.74 - 3.9	2.0	1.4	2.5 - 6.0	4.4	1.2
SO_2, ppm	123 - 730	553	110	183 - 1,924	596	240
NO_x, ppm	306 - 460	386	49	288 - 552	446	64
CO, ppm	10 - 4,900	477	966	10 - 4,540	599	1,409
THC, ppm	6.7 - 12.7	8.2	1.9	1.5 - 10.0	3.5	1.1

exits the kiln distributed in the lime product (~9%), baghouse dust (~27%), and stack gas (~64%).

An elemental material balance was performed for 21 elements. Balance results show no difference for baseline and waste fuel conditions for distribution of metals in the kiln process. Also the majority of mass entering the kiln is contributed by the limestone feed (typically 80-100%) except for zinc which has 42% in the limestone and 53% in the waste fuel. The mass exiting the kiln is distributed between the lime product and baghouse dust (approximately 50-90% in product and 10-45% in dust). Magnesium and calcium had mass rates (to or from kiln) of approximately 2,500 kg/hr. Sodium and iron mass rate were approximately 20 kg/hr. All other elements had mass rates less than 5 kg/hr.

Baseline vs. Waste Fuel and Kiln Operation

Emissions were evaluated under baseline and waste fuel conditions. For the pollutants listed in Table 5, HCl, NO_x and THC showed a significant difference in stack emissions under baseline and waste fuel conditions. For the POHC's, only methylene chloride and toluene showed a minor difference (increase) from baseline to waste fuel conditions. All remaining POHC's showed no significant difference in baseline vs. waste fuel emissions.

As described previously, the kiln operation fluctuated as indicated by CO and SO_2 emission variations during waste fuel burning. Kiln fluctuations were caused by several items including nonconstant fuel rates, product rushes, clumps of coke fed to kiln accidentally, and operator inexperience with burning waste fuel. The fluctuation resulted in occasional kiln O_2 increases and stack gas SO_2 decrease causing a poorer quality lime product most likely due to excess sulfur in the product. The following items were identified as ways to improve operation at this kiln under waste fuel conditions:

1. Change waste fuel burner configuration such that at low waste fuel rates the waste fuel is mixed with the coke to maintain a flame.
2. Decrease the fan speed (i.e., reduce the draft) to lower the O_2 in the kiln resulting in lower sulfur in product and higher sulfur in the stack.

TABLE 6. CHLORINE AND SULFUR MATERIAL BALANCE

Run number	Percent to kiln: Coke	Percent to kiln: Waste fuel	Percent to kiln: Limestone feed	Total mass in, kg/hr	Percent from kiln: Lime product	Percent from kiln: Baghouse dust	Percent from kiln: Stack gas	Total mass out, kg/hr	Material balance closure, %
Chlorine									
Baseline[a]	4	0	96	23	47	52	1	13	55
Waste fuel[b]	5	2	93	21	34	65	1	20	105
Sulfur									
Baseline[a]	100	0	NA	59	8	29	63	91	73
Waste fuel[b]	99	1	NA	54	10	25	65	70	77

[a] Average values of baseline Runs 1-3.

[b] Average values of waste fuel Runs 4-8.

FIELD TESTS OF INDUSTRIAL BOILERS COFIRING HAZARDOUS WASTES

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ABSTRACT

Thirteen field emission tests have been performed on eight industrial boilers cofired with conventional fuels and hazardous wastes. The U.S. Environmental Protection Agency (EPA) sponsored the tests to evaluate the effectiveness of industrial boilers for hazardous waste thermal destruction while recovering useful energy. Five initial tests were made on a wide range of waste type/boiler design combinations to quantify emissions representative of current industry practices. For the second series of tests, boilers firing waste streams spiked with a mixture of carbon tetrachloride, chlorobenzene, and trichlorethylene were tested to extend the data base for chlorinated wastes and facilitate intrasource comparisons. Principal organic hazardous constituents (POHC's) in the flue gas were quantified using two extractive sampling trains. Volatile compounds were absorbed on two Tenax traps in the volatile organic sampling train (VOST). Semivolatile compounds were absorbed on XAD-2 sorbent in a modified Method 5 train. The sampling protocol also included continuous monitor measurement of stack O_2, CO, CO_2, NO_x and total hydrocarbons; extractive train samples of HCl; and grab samples of the conventional and waste fuels and ash streams. Post-test analyses of the inlet fuels and the outlet stream samples were done with gas chromatography/mass spectrometry to quantify the destruction and removal efficiency of POHC's. Results for the thirteen tests are discussed in this paper. Specie destruction and removal efficiency (DRE) ranged from 99.5 to >99.999 percent. The mass weighted destruction efficiency for all RCRA Appendix VIII compounds was 99.998 percent. Products of incomplete combustion (PIC's) were observed in concentrations one order of magnitude greater than measured breakthrough POHC's.

INTRODUCTION

Many hazardous wastes have sufficiently high heat of combustion to be candidates for cofiring with conventional fuels in industrial boilers. Cofiring can be economically and environmentally advantageous to other disposal/destruction options while meeting the Resource Conservation and Recovery Act (RCRA) goal of resource recovery. The benefits of cofiring include partial displacement of conventional fuels, and use in existing industrial boilers where incinerators are not available. Although boiler cofiring is not currently regulated, the need for inclusion in RCRA provisions is currently being studied by EPA. EPA sponsored the tests discussed in this paper to quantify the waste destruction potential of industrial boilers. To obtain results representative of current or potential industrial practice, a broad range of boiler designs and waste types was selected for testing (1). Eight sites were tested encompassing thirteen tests of which the initial three were reported at the Ninth Symposium(2).

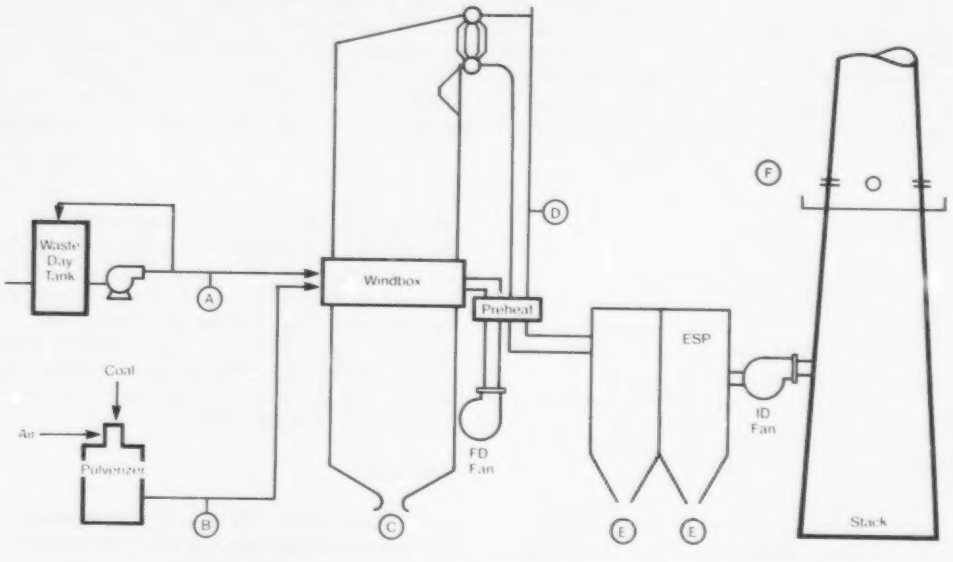
APPROACH

Candidate sites were screened based on representativeness of the boiler design and wastes being fired, and the availability and accessibility for cofiring tests. Within this context, preference was given to sites which were regarded as more challenging in attaining a high level of waste destruction. Table 1 summarizes the eight test sites and thirteen test series. Sites A and H were solid-fuel-fired and were equipped with a cyclone and electrostatic precipitator, respectively. Site G was fired with chlorinated hydrocarbons without auxiliary conventional fuel and was equipped with two scrubber columns for HCl recovery and cleanup. The selected sites spanned a broad range of design and operating conditions: firetube and watertube designs; capacities from 1.1 kg/s (8,500 lb/hr) to 32 kg/s (250,000 lb/hr); gas, oil, coal and wood firing; loads from 25 to 100 percent of rated capacity; wastes ranging over an order of magnitude in heat of combustion; and residence time and heat release variations over an order of magnitude. To extend the range of waste destruction characteristics tested, the wastes at site E-H were spiked with carbon tetrachloride and, in most cases, monochlorobenzene and trichloroethylene.

The nominal test series involved an initial conventional fuel baseline test to characterize unit operation and emissions in the absence of waste firing, and triplicate cofiring runs. For these runs, the unit load was held constant to enable replicate comparisons of results. In most other respects, routine operational variations such as excess air levels and waste flowrates were tolerated to obtain results representative of normal operation.

The major inlet and outlet streams were sampled and analyzed as shown in Figure 1, for the case of a coal-fired unit, and boiler operational data was taken to characterize performance with and without waste firing. Details on the protocol are given in (1). Waste and fuel grab samples were taken approximately every hour, composited, and analyzed in the laboratory for ultimate and proximate analyses, chloride content, and POHC concentration. Bottom and hopper ash composite samples were analyzed for chlorides, POHC's, and carbon content. The major sampling was conducted at the stack where the following samples were taken:

- Continuous monitor analyses of O_2, CO, CO_2, NO_x, and UHC



A — Liquid Waste Grab Samples (Composite)
B — Fuel Grab Samples (Composite)
C — Boiler Bottom Ash Grab Samples (Composite)
D,F — Stack Emissions
E — Particulate Collector Hopper Ash

Figure 1. Sampling schematic.

TABLE 1. BOILER DESIGN AND OPERATING CHARACTERISTICS

				Operation			
Site	Boiler† Type and Capacity kg/s (10^3 lb/hr)	Primary Fuel	Waste (percent heat input) POHC's*	Steam Load kg/s (10^3 lb/hr)	Percent O_2	Residence time (s)	Heat release kW/m^3 (10^3 Btu/ft^3h)
A	WT Stoker 1.26 (10)	Wood waste	(40) creosote	1.26 (10)	6-16	1.2	300 (29)
B	FT 1 Burner 1.1 (8.5)	Gas	Alkyd wastewater	0.26 (2)	4-6	0.8	750 (72)
C	WT 6 Burner 29 (230)	Gas	(38) phenol/cumene	7.4 (59)	10	2	78 (7.5)
D	WT 4 Burner 11 (90)	Oil	(26) xylene, PCE	8.8 (70)	4-6	1.1	400 (39)
			(48) toluene, BCEE	5.7 (45)	6	1.3	240 (23)
E	WT 1 Burner 14 (110)	Oil	(28) MMA, CCl_4, Cl_ϕ, TCE	6.9 (55)	7	0.7	520 (50)
			(42) MMA, CCl_4, Cl_ϕ, TCE	5.0 (40)	6	1.0	350 (34)
			(19) MMA, CCl_4, Cl_ϕ, TCE	10 (80)	7	0.5	770 (74)
		Gas	(33) MMA, CCl_4, Cl_ϕ, TCE	7.2 (57)	6	0.8	470 (45)
			(52) MMA, toluene	5.6 (44)	7	1.1	370 (36)
F	WT 2 Burner 7.6 (60)	Oil	(10) solvent, CCl_4, Cl_ϕ, TCE	4.0 (32)	7-11	2	110 (11)
G	FT 1 Burner 4.0 (32)	NA	(100) CCl_4, chlorinated hydrocarbons	1.8 (14)	8	0.4	820 (79)
H	WT T-Fired 32 (250)	Coal	(3) MeA, CCl_4, Cl_ϕ, 1,1,1-TCA	32 (250)	6	2	180 (17)

*PCE = tetrachloroethylene; BCEE = bis(2-chloroethyl)ether; MMA = methylmethacrylate; Cl_ϕ = monochlorobenzene; TCE = trichloroethylene; MeA = methylacetate; 1,1,1-TCA = 1,1,1-trichloroethane

†WT = watertube; FT = firetube

- Volatile organics extractive samples by the Volatile Organic Sampling Train (VOST) (3)
- Semivolatile organics and particulates by the modified Method 5 extractive sampling train (4)
- Chlorides by a Method 6 extractive sampling train
- C_1-C_6 hydrocarbons by a gas bomb grab sample and gas chromatograph analyses

Each test required approximately 6 hours of run time. Post-test analyses of the volatile and semivolatile samples collected on resin traps were done by gas chromatography/mass spectroscopy (GC/MS). Waste destruction and removal efficiencies were computed based on feed and stack mass flowrates quantified in the samples:

$$DRE = (M_{feed} - M_{stack})/M_{feed} \times 100$$

Constituents appearing in the stack which were not identified in the feed or other inlet stream were identified as products of incomplete combustion (PIC's).

RESULTS

Table 2 summarizes POHC-specific DRE results. Calculated DRE's are based on blank corrected emission rates measured during cofiring. Therefore, credit is not given for emission of POHC's measured during baseline tests. Results indicate a wide range in DRE's from 99.5 to >99.999 percent. The mass weighted average DRE for all POHC's was 99.998 percent. Although the average DRE for each POHC was generally greater than 99.99 percent, some emission measurements resulted in DRE's below this level, the current RCRA incinerator standard. These low DRE's often coincided with unsteady boiler operation and burner combustion instability. For example, low DRE's for carbon tetrachloride, chlorobenzene, and trichloroethylene are generally attributable to site F. Improper burner settings at this site resulted in coking of the burner nozzle, fuel impingement on burner throat, and occasionally high levels of combustible CO and soot emissions.

Low DRE's for site E methylmethacrylate were measured during few tests characterized by instability in waste

TABLE 2. SUMMARY OF POHC DRE RESULTS

POHC	Inlet (ppm) $\left[\frac{M_W}{M_T}\right] \times 10^3$	Emission rate µg/s	Mass average DRE percent	DRE range percent	Site
Carbon tetrachloride	1.0-50	1-460	99.998	99.97-99.999	E, F, G, H
Trichloroethylene	0.78-12	28-470	99.998	99.98-99.999	E, F
1,1,1 Trichloroethane	0.82-0.96	<0.3-17	99.994	99.98-99.999	H
Chlorobenzene	0.13-7.5	3.6-190	99.998	99.97-99.999	E, F, H
Phenol	0.23-21	<0.6-190	99.999	99.5-99.999	A, C
Pentachlorophenol	0.88-2.4	<3.2-44	99.998	99.985-99.998	A
Tetrachloroethylene	8.0-90	510-1,400	99.998	99.994-99.999	D
Bis(2-chloroethyl)ether	18-20	<3-6.8	>99.999	>99.999	D
Toluene	0.46-450	29-8,800	99.998	99.90-99.999	B, D, E, F
Fluorene	1.8-3.0	<0.6-34	99.996	99.986->99.999	A
Naphthalene	2.2-7.6	25-150	99.983	99.946-99.988	A
Methylmethacrylate	7.9-62	17-8,300	99.991	99.95-99.999	E
2-4 Dimethylphenol	0.12-0.52	<3.2-13	>99.983	99.96->99.99	A
Epichlorohydrin	160-210	<2	>99.999	>99.999	G
Bis(2-chloroisopropyl)ether	400-540	<2	>99.999	>99.999	G
	0.12-540	<0.6-8,800	99.998	99.5->99.999	

feedrates and insufficient combustion air. These operating conditions led to several high CO and smoke emission episodes. Wood-fired stokers, such as the site A boiler, are typically high excess air and high CO emitters. These conditions result from the physical properties of wood waste (e.g., wood chip size and high moisture content), combustion cooling by very high excess air levels and inefficient fuel-air/mixing of combustion on a fuel bed. Site A DRE's were generally below 99.99 percent. Table 3 illustrates this site dependence more clearly. An attempt to correlate DRE's with CO emissions was not successful, however. It is likely that this was in part due to insufficient emission measurements during periods of high CO or smoke emissions.

Figure 2 illustrates an apparent DRE dependence on POHC concentration in the waste fuels. The data are based on mass average DRE's for all POHC's at each site. Therefore, included are DRE results for other organics not listed in Table 3. The data indicate that higher DRE's were obtained with higher POHC firing rates. This result suggests that the amount of POHC breakthrough is independent of the POHC concentration in the waste fuel. One factor that contributes to this trend is the high DRE's for semivolatile organics (phenol, BCEE, epichlorohydrin, and bis(2-chloroisopropyl)ether) that were present at high concentrations in waste fuels of sites C, D, and G. Results for other nonhazardous organics present at the high concentrations in site E waste fuel also showed high DRE's. A second factor, is the background contamination from sampling and analysis techniques which tends to be more significant at low POHC emissions. Also important is the contribution of volatile organics from fossil fuel combustion.

Quantitation of PIC emissions was based on the detection of organic priority pollutants not found in the waste fuel. Figure 3 illustrates the relationship between the sum of total PIC's, halogenated and nonhalogenated organics, versus the test average DRE for site D through H. The data suggest that the lower the quantity of POHC breakthrough (i.e., higher DRE) the lower the total quantity of PIC's. Therefore, higher POHC DRE's are also likely to result in lower PIC emissions. On the average, PIC emissions were one to two orders of magnitude greater than the total quantity

TABLE 3. SUMMARY OF SITE DRE RESULTS

				POHC DRE percent				
Site	DRE range	CCl$_4$	TCE*	Cl$_\phi$	PCP†	PCE††	Toluene	Average DRE
A	99.5-99.999	--	--	--	99.988	--	--	99.98
B	99.991	--	--	--	--	--	99.98	99.98
C	99.998->99.999	--	--	--	--	--	--	99.9990
D	99.994-99.9996	--	--	--	--	99.998	99.9994	99.9990
E	99.95-99.9995	99.999	99.998	99.998	--	--	99.997	99.995
F	99.90-99.999	99.98	99.996	99.98	--	--	99.95	99.98
G	99.995->99.999	99.998	--	--	--	--	--	99.9996
H	99.97-99.999	99.988	--	99.992	--	--	--	99.991
	99.5->99.999	99.998	99.998	99.998	99.988	99.998	99.998	99.998

*TCE = trichloroethylene
†PCP = pentachlorophenol
††PCE = tetrachloroethylene

FIELD TESTS OF INDUSTRIAL BOILERS AND INDUSTRIAL PROCESSES DISPOSING OF HAZARDOUS WASTES

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ABSTRACT

Two industrial boilers were tested to determine their hazardous waste destruction performance. The tests are part of a research program conducted by the EPA to evaluate a spectrum of representative boiler types that are currently being used for hazardous waste disposal. These boiler tests provide destruction efficiency (DE) results as the primary performance parameter. Waste materials typically burned in the boilers were spiked with a standard test mixture containing components expected to vary in incinerability. The standard test mixture provides the EPA with a means of comparing the thermal destruction performance among several boilers.

The boilers were operated at a single steady state load of 80% of design capacity with operator settings of excess air and feed rate controlled by normal operating procedures. A series of three background runs and three waste feed runs were conducted at the prescribed boiler load. Additional sampling runs were required during Boiler No. 1 testing to evaluate NO_x control with and without staged combustion.

The destruction efficiencies of ten POHCs (principal organic hazardous constituents) were determined at low and high waste to fuel ratios. No correlation was found of destruction efficiency with potenital incinerability indicators (carbon monoxide and total hydrocarbons). Only two products of incomplete combustion (PICs) were identified during the two boiler tests. Numerous organic species not detected in the feed were detected in the emissions but these are believed degradation products of the sample collection media. Staged combustion NO_x control was used when burning nitrogenous waste and was found to reduce NO_x emissions. Heavy metals concentrations in the emissions when burning wastes were compared with concentrations when burning the baseline fuel.

INTRODUCTION

Two industrial boilers were tested to determine their hazardous waste destruction performance. The tests are part of a research program conducted by the EPA to evaluate a spectrum of representative boiler types that are currently being used for hazardous waste disposal.

These boiler tests provide destruction efficiency (DE) results as the primary performance parameter. Waste materials typically burned in the boilers were spiked with a standard test mixture containing components expected to vary in incinerability. The standard test mixture provides the EPA with a means of comparing the thermal destruction performance among several boilers.

The two boilers epitomize considerable diversity in waste disposal goals and waste feed characteristics. Wastes are burned in Boiler No. 1 primarily to dispose of a hazardous waste and not for appreciable fuel savings. Waste to fuel ratios determined on a heat input basis were 0.09 to 1, meaning that only 8% of the energy was supplied by the waste. There is no clearly identifiable waste to fuel ratio to report for Boiler No. 2 because a substantial amount of the waste burned is off specification fuel. During the test, No. 6 fuel oil contributed less than 50% of the input energy and it is clearly the intent to obtain substantial fuel savings by burning either wastes or off specification fuels. Table 1 summarizes significant differences in the design and waste disposal characteristics of the two boilers. Boiler No. 1 represents a class of boilers disposing of a specific waste that is well characterized with respect to knowledge of the composition and of the expected volume of waste. Boiler No. 1 also represents cofiring of a liquid waste with a gaseous fuel. Boiler No. 2 represents a class of boilers that are not limited to a specific waste stream. Variation in fuel and waste composition is the expected norm for Boiler No. 2. Boiler No. 2 cofires liquid wastes and off specification fuels with No. 6 fuel oil. Specific components of the liquid wastes are not always known.

PURPOSE

The two boilers were tested by similar procedures. The principal goals were:

- the identification of principal organic hazardous constituents (POHCs) in the feed and the extent of their destruction,
- the correlation of destruction efficiency with boiler operating settings with the boiler operating at steady state,
- the fate of other feed components such as chlorine, heavy metals, and fuel bound nitrogen,
- the identification of products of incomplete combustion (PICs), and
- the correlation of candidate incinerability indicators with destruction efficiency.

The objectives of this report are to (1) report and compare the results of the two boiler tests and (2) identify and highlight specific thermal destruction measurement limitations that were encountered during the test programs.

TABLE 1. BOILER DESIGN AND OPERATING DATA

	Boiler No. 1	Boiler No. 2
Manufacturer	FW	CE
Model number	AG252	VU-10
Heat exchanger	-----Water Tube-----	
Design fuel	Gas	No. 6 oil
Design excess air	3%	3%
Design steam rate, lb/hr	68,000	60,000
Steam temperature, ^{o}F	353	406
Steam pressure, psig	250	125
Design fuel heating value, Btu/lb	23,000	18,500
Waste heating value, Btu/lb	10,600	17,700

FW - Foster Wheeler
CE - Combustion Engineering

APPROACH

The boilers were operated at a single steady state load of 80% of design capacity with operator settings of excess air and feed rate controlled by normal operating procedures. A series of three background runs and three waste feed runs were conducted at the prescribed boiler load. Additional sampling runs were required during Boiler No. 1 testing to evaluate NO_x control with and without staged combustion.

Characteristics of the boiler feed streams and procedures for sampling and analysis are described in the following sections.

Feed Characteristics

Boiler No. 1 was fired with fuel gas and a liquid nitrogenous waste. The fuel gas was predominantly natural gas with small amounts of a waste gas not substantially different from natural gas. The nitrogenous waste was predominantly nitrobenzene with the balance consisting of benzene, aniline and water. Waste to fuel ratio on a weight basis averaged 0.2 to 1 at a liquid waste feed rate of 0.6 gpm (362 lb/hour).

Initial boiler design included two vertically oriented ring burners. The burner system had been modified by the addition of steam atomized liquid burners. The boiler controls had been modified to achieve staged combustion during periods of liquid waste firing by restricting air flow to the bottom set of liquid and gas burners. Air not supplied to the lower burners was directed to the upper burner to maintain the total air flow necessary for boiler excess air requirements. Two series of sampling runs were conducted to compare NO_x emissions with and without combustion control. To do this, the automatic controls for restricting air to the lower burners was disabled. Balanced air flow to each set of burners was thus maintained to establish the "unstaged" combustion effect.

Boiler No. 2 normally burns one of two fuels that are classified according to viscosity. Generic designations are "heavy oil" for the high viscosity liquids and "light oil" for the low viscosity liquids. Various blends can be created of No. 6 fuel oil with various combustible liquids such as recycled solvents, alcohols, mineral spirits and substandard fuel oils. The blends vary in composition according to availability. Boiler No. 2 is capable of burning two different blends simultaneously and this option was chosen for testing. The boiler has four burners oriented horizontally on the front face of the boiler. The heavy oil and light oil were not substantially different in heating value. Therefore, approximately equal amounts of each feed stream could be burned and a set of two burners each were set aside for each feed type. Heavy oil was steam atomized and light oil was air atomized.

Waste liquids were spiked with a standard test mixture: carbon tetrachloride, 1,1,2-trichloroethylene, monochlorobenzene, and toluene. To protect the boiler surfaces from chloride corrosion damage, quantities were limited to one weight percent as chlorine of the total fuel and waste. Selection of test mixture components is an attempt to provide a broad range of incinerability of hazardous compounds as postulated from relative heats of combustion (1). Actual total chlorine in the boiler feed was 0.7 weight percent for both boiler tests. The standard test mixture was added to the light oil of Boiler No. 2. Table 2 shows typical feed stream compositions for the two boilers.

Sampling

Feed and emissions samples were collected simultaneously. Boiler No. 2 was operated with two liquid feeds during testing and samples of each were collected, composited and analyzed separately. One sample per run was collected of Boiler No. 1 feed gas.

Emissions were sampled with three sampling trains:

- the volatile organic sampling train (VOST) for volatile organics,
- the modified EPA Method 5 train (MM5) for semi-volatile organics and metals, and
- the EPA Method 5 train for HCl and metals.

TABLE 2. FEED COMPOSITIONS

	Weight % of fuel + waste	
	Boiler No. 1	Boiler No. 2
Fuel gas	83.8	not used
Standard test mixture		
Carbon tetrachloride	0.3	0.5
Trichloroethylene	0.3	0.4
Monochlorobenzene	0.5	0.4
Toluene	0.5	2.0
Liquid waste		
Nitrobenzene	13.4	not detected
Phenol	not detected	11.8
Aniline	0.4	not detected
Benzene	0.3	0.2
m&p-Xylene	not detected	4.3
o-Xylene	not detected	0.6
Water	0.5	1.1
Small quantities of typical fuel oil components and solvents	not used	balance
Total POHCs detected	15.7	20.2

The VOST train collects the more volatile organics from a filtered, precooled gas stream by adsorption on Tenax resin. The gas was passed through two sorbent traps in series. The first trap contained Tenax and the second trap contained a layer of Tenax followed by a layer of charcoal. Protection from sample contamination by trace organics dictates strict protocols for cleaning glassware, for sealing glass joints without the use of grease, and air tight sealing of sorbent traps during storage and shipment. Minimum leakage at glass joints was assured by strict adherence to leak check procedures and guidelines. The samples were recovered from the Tenax by thermal desorption and analyzed by gas chromatography/mass spectrometry procedures.

The modified Method 5 train collects organics with boiling points above a nominal 100°C level by adsorption on XAD-2 resin. An EPA Method 5 train was modified by addition of a sorbent trap ahead of the impinger train. Temperature of the sorbent traps was controlled so as not to exceed a 20°C exit temperature. Organics collected in traps were recovered by solvent extraction from which the sample-containing solvent was analyzed by GC/MS after appropriate concentration or dilution. Some samples were prescreened by GC/FID to determine expected calibration ranges for the GC/MS.

The EPA Method 5 train was used to collect HCl samples at a single point on the duct traverse. The HCl was absorbed in 1.0 molar solution of sodium acetate and the sodium acetate combined with filter extract was analyzed by ion chromatography. Metals were also collected by this sampling train during Boiler No. 1 testing. Boiler No. 2 testing utilized a second EPA Method 5 train to collect particles for metals analysis. Method 5 procedures were employed.

PROBLEMS ENCOUNTERED

Feed Preparation

Specific quantities of the standard test mixture (carbon tetrachloride, trichloroethylene, monochlorobenzene, and toluene) had to be added to the plant wastes and mixed well enough to attain consistent feed composition throughout the test period. A premixed batch was prepared in enough quantity to provide all of the feed mixture needed. Examination of sample mixtures prepared prior to testing showed that only one liquid phase was present. However, variation in density at different tank levels was observed for the Boiler No. 2 liquid feed mixture. Hence, constant circulation with rapid turnover of the stored liquid was required to minimize stratification.

Ambient Air Contamination

The VOST sampling train is equipped with a charcoal filter to trap organics of the ambient air when the train is pressurized for leak testing. It was found during Boiler No. 1 testing that organics in the ambient air exceeded organic emissions. The modified Method 5 train was not equipped with a similar air cleaning filter until Boiler No. 2 testing. Evidently, there were no POHCs or PICs in the ambient air in detectable quantities during Boiler No. 1 testing that would contaminate modified Method 5 samples. Nevertheless, as a precaution, all ambient air to the organic sampling trains will be filtered during future test programs.

Identification of Products of Incomplete Combustion (PICs)

Comparisons of analytical results of all test runs, both waste feed and baseline runs, consistently show the same compounds in the extracts from XAD-2 emission sampling traps. The same compounds are found in the extracts from field blanks. These compounds are attributed to degradation/leaching of XAD-2 resin and not to PIC formation. The collection method (XAD-2 resin) followed by fused silica capillary chromatography with mass spectrometer detection allows for excellent determination of the destruction efficiency of POHCs, but the identification and quantitiation of PICs must be approached with caution.

Benzene Interference

Benzene analysis indicates that destruction efficiencies were less than 99.99% during both Boiler No. 1 and Boiler No. 2 testing. Statistical treatment of Boiler No. 1 test data showed that benzene emission levels during the waste feed runs were not significantly different from the baseline runs. We thus attributed benzene concentrations in the emissions to a benzene background in the Tenax sampling trap. Benzene levels during Boiler No. 2 testing were an order of magnitude greater in the baseline runs than in the waste feed runs despite the fact that no benzene was detected in the baseline fuel (No. 6 fuel oil). This is a different set of circumstances than the Boiler No. 1 case and a phenomena we are unable to explain. Unfortunately, destruction efficiency of benzene was not measureable during the two boiler tests due to the apparent benzene interferences.

RESULTS

Program accomplishments were as follows:

- Destruction efficiencies of ten POHCs (principal organic hazardous constitutents) were determined.
- Hazardous waste disposal performance at low and high waste/fuel ratios were compared.
- Data for correlation of destruction efficiency with operating parameters were provided.
- Very few PICs (products of incomplete combustion) were detected and identified.
- NO_x emissions when burning a nitrogenous waste was compared with and without combustion control.
- Heavy metals emission data were collected.
- Chloride mass balance calculations showed greater than 100% closures (127% for Boiler No. 1 and 108% for Boiler No. 2).

Boiler No. 1, which is used to solve a specific waste disposal problem without large fuel savings, was successful in destroying the plant's wastes at the concentrations fed to the boiler. Boiler No. 2, which capitalizes on various waste disposal opportunities to accomplish significant fuel savings, realized acceptable DEs except for xylenes for relatively high concentrations of POHCs in the feed.

Destruction Efficiency

Destruction efficiency (DE) was determined by analyzing for POHCs of interest in the feed and in the emissions, calculated as follows:

$$DE = 100\ (POHC_{in} - POHC_{out})/POHC_{in}$$

The POHCs include the components of the standard test mixture and the major hazardous compounds in the waste feed. DE requirements of 99.99% were exceeded for all compounds except xylenes (Table 3). Better than 99.99% DE was accomplished at POHC levels in the feed of 16% (Boiler No. 1) and 20% (Boiler No. 2).

Correlation with Boiler Operation

The test programs provide an opportunity to look for a correlation of easily measured boiler parameters with destruction efficiencies. The purpose is to develop indicators that could substitute for the time consuming and costly destruction efficiency tests. Two of the indicators often mentioned are carbon monoxide (CO) and total hydrocarbon concentrations in the flue gas. CO and total hydrocarbon (THC) concentration did not correlate with destruction efficiency at the low levels of emissions concentrations encountered. A possible explanation is that even the low levels of CO and THC represent orders of magnitude higher concentrations than the concentrations of POHCs in the emissions. For example; the highest CO concentration observed, 242 ppmv, reflects a feed carbon to unoxidized carbon ratio of 430 to 1 whereas a 99.99% destruction efficiency of a POHC represents a 10,000 to 1 ratio of feed POHC to emissions POHC.

TABLE 3. DESTRUCTION EFFICIENCY

POHC	Boiler No. 1 Staged combustion	Boiler No. 1 Unstaged combustion	Boiler No. 2
Standard test mixture			
Carbon tetrachloride	99.997	99.997	99.999
Trichloroethylene	99.999	99.999	99.999
Monochlorobenzene	99.998	99.998	99.999
Toluene	99.997	99.998	99.999
Liquid waste			
Nitrobenzene	99.999	99.999	not detected
Phenol	not detected	not detected	99.999
Aniline	99.998	99.998	not detected
o-Xylene	not detected	not detected	99.958
m&p-Xylene	not detected	not detected	99.947

Values beyond three decimal places were ignored.

Products of Incomplete Combustion (PICs)

PICs were found in the Boiler No. 2 emissions and consisted of substituted phenols (methyl butyl phenol, dimethyl phenol). Their presence is probably due to the high concentration of phenol in the boiler feed. The substituted phenols are not the XAD-2 artifacts that were discussed in the Problems Encountered section.

NO_x Control When Burning Nitrogenous Waste

Gas fired Boiler No. 1 had been modified to accommodate cofiring of a mixture of nitrobenzene, aniline and benzene with fuel gas. Included in the modifications were changes in air distribution to the burner to provide staged combustion NO_x control. Testing confirmed that staged combustion was effective in controlling NO_x emissions (Figure 1). NO_x emissions were 73% less than the equivalent organic nitrogen present in the liquid waste. Organic nitrogen compounds were not detected in the fuel gas. Corrected for background emissions, which are all derived from combustion air, estimated NO_x emissions were 78% less than the organic nitrogen in the feed. Without staged combustion, organic nitrogen was lowered by only 24% or by an estimated 28% if corrected for baseline emissions.

Fate of Metals

Particle catches were analyzed for specific heavy metals. Particulate matter emissions from Boiler No. 1 were quite low and specific metal concentrations exceeded minimum detectable limits only slightly if at all. Also, differences between liquid waste runs and background runs were not distinguishable for most metals. Mercury and lead were the only exceptions. It was concluded that heavy metals emissions from Boiler No. 1 were not a significant problem.

Boiler No. 2 feed streams, both the No. 6 fuel oil and the waste solvents, contained significant amounts of several of the heavy metals. Strainers were used to remove bulk quantities of solids from the boiler feed streams. This is usual practice with fuels of the type used. Thus, metals concentrations in the filtered feed streams emulate typical practice. The two feed streams were examined for fourteen metals. Nine metals were found in excess of one ppmw (Table 4). Significant levels of vanadium, nickel, zinc, lead and cobalt were found in the baseline fuel (No. 6 fuel oil). Substantial quantities of vanadium, zinc and lead in the light oil added to the potential for having significant concentrations of these metals emitted to the atmosphere. Also, the light oil contained a significant level of manganese. Since about one third of the total boiler feed during the waste disposal runs was baseline No. 6 fuel oil, it was of interest to know whether there were significant differences between baseline emissions and waste firing emissions. Waste firing resulted in higher emissions of zinc, lead, cadmium, copper, manganese, chromium and cobalt. Vanadium and nickel were the only metals in significant concentrations in No. 6 fuel oil that did not show an increase. Of the metals showing an increase, concentration ranges during waste firing were as follows:

zinc: $>1000\ \mu g/m^3$
lead: $>1000\ \mu g/m^3$
cadmium: $100 - 1000\ \mu g/m^3$
chromium $10 - 100\ \mu g/m^3$
copper: $10 - 100\ \mu g/m^3$
manganese: $10 - 100\ \mu g/m^3$
chromium: $10 - 100\ \mu g/m^3$
cobalt: $10 - 100\ \mu g/m^3$

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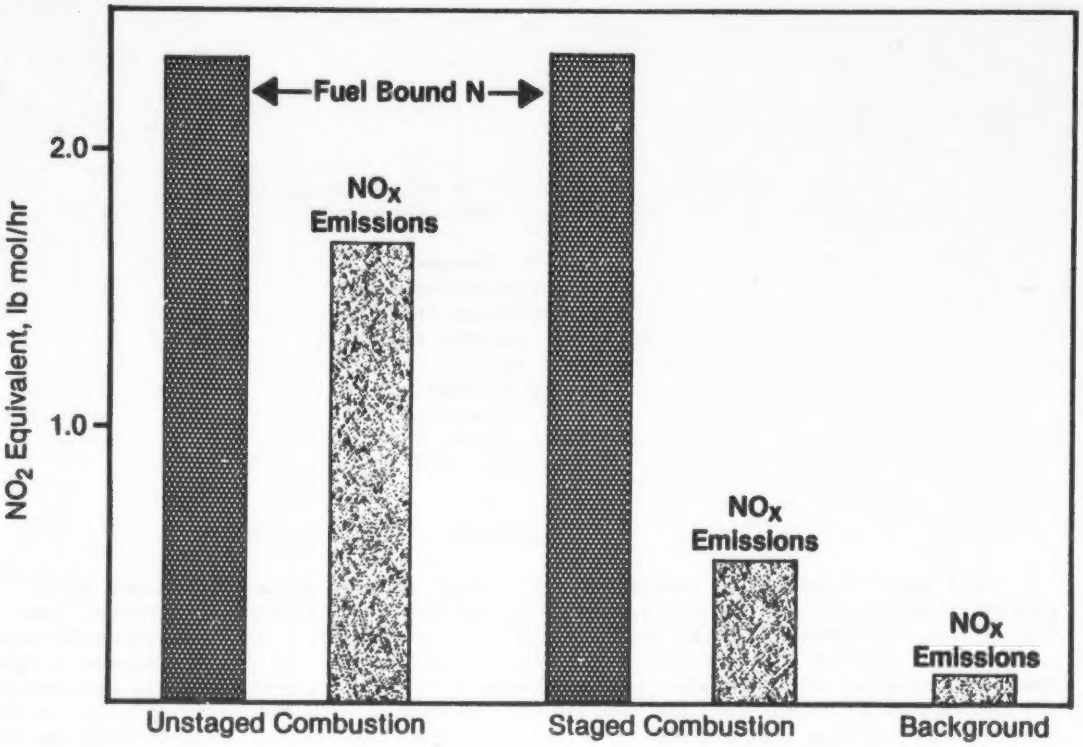

Figure 1. Boiler No. 1 NO_x control performance.

TABLE 4. TRACE METALS ANALYZED

	Greater than one ppm in feed?		Greater than one ppm in feed?
Zinc	Yes	Chromium	Yes
Lead	Yes	Cobalt	Yes
Vanadium	Yes	Arsenic	No
Nickel	Yes	Mercury	No
Cadmium	Yes	Antimony	No
Copper	Yes	Selenium	No
Manganese	Yes	Strontium	No

SUMMARY OF FIELD TESTS FOR AN INDUSTRIAL BOILER DISPOSING OF HAZARDOUS WASTES

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ABSTRACT

This paper presents the results of field tests of a North American Model 3200X package fire-tube boiler burning a mixture of toluene and chlorinated solvents. Two fuel blends were tested. Blend #1 contained 98 wt % toluene, 1 wt % trichloroethylene, and 0.5 wt % each of chlorobenzene and carbon tetrachloride. Blend #2 differed in that the trichloroethylene concentration was increased to 2 wt % and the toluene concentration was reduced to 97 wt %. Flue gas samples were collected with the VOST, Modified Method 5, and Method 23 sampling systems. The VOST and Modified Method 5 samples were analyzed by GC/MS while the Method 23 samples were analyzed by on-site GC. Continuous analyzers were used to measure the oxygen, carbon monoxide, and nitrogen oxides content of the flue gas.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) regulates the destruction of hazardous wastes in incinerators requiring a Destruction and Removal Efficiency (DRE) of 99.99 percent (%) for the Principal Organic Hazardous Constituents (POHCs) that are present in the waste. Particulate matter emissions are limited to 0.08 grains/dry standard cubic foot (gr/dscf) corrected to 12% carbon dioxide (CO_2), and hydrogen chloride (HCl) emissions are limited to 4 pounds per hour (lb/hr) or 1% of the uncontrolled HCl whichever is greater. Processes which primarily produce energy and coincidentally burn hazardous wastes are currently exempt from hazardous waste destruction regulation. This includes processes such as industrial boilers, kilns, blast furnaces, process heaters, and ovens.

The EPA is investigating the need for regulating hazardous waste combustion in thermal industrial processes. A Regulatory Impact Analysis (RIA) is being conducted to determine the need for and effects of regulating these processes. Part of the input needed for the RIA is information on the ability of these processes to destroy hazardous wastes.

This paper presents data obtained from tests of a fire-tube boiler burning 100% hazardous waste. The project was sponsored by the EPA Office of Solid Waste (OSW). The OSW Project Manager was Mr. Marc Turgeon. The project was conducted under contract from the EPA Industrial Environmental Research Laboratory (IERL) in Cincinnati, Ohio, who provided the technical direction. Mr. Robert A. Olexsey was the IERL Technical Manager. Engineering-Science (ES) was the prime contractor for the project and was responsible for overall project coordination; collection of the Volatile Organic Sampling Train (VOST), Modified Method 5 (MM5), and HCl samples; and report preparation.

ES was assisted by SYSTECH Corporation, who was responsible for obtaining the test site, coordinating with the plant, and conducting EPA Proposed Method 23 (M23) sampling. Analyses of the VOST and MM5 samples were performed by Research Triangle Institute.

PURPOSE

This test was one of a matrix of about 14 tests conducted by IERL to obtain DRE data for industrial boilers. The matrix included a wide range of boiler sizes and types. This particular test was to provide DRE data for a small fire-tube boiler. Most of the other tests involved co-firing of hazardous waste with the normal boiler fuel. This test, however, was designed to determine DRE for 100% hazardous waste burning, a practice that is known to be used by some facilities.

There was a secondary purpose of this test program: to compare the results obtained with VOST and MM5 to those obtained with M23.

APPROACH

Boiler Description

All field testing was accomplished on a North American Model 3200X package fire-tube boiler. This unit is referred to as an "Ohio Special" because it has only 358 ft^2 of flue gas to water heat exchange surface, and therefore does not require a full-time licensed operator. "Ohio Specials" probably represent a worst-case situation for destroying hazardous wastes in fire-tube boilers. With a high heat release of 92,000 Btu/hr ft^2 and a high liberation rate of 164,400 Btu/hr ft^3, it is expected that high combustion temperatures and very short retention times occur in the furnace of the test unit. However, the nonconservative design of an "Ohio Special" may also have some advantages when well controlled combustion is desirable. It was discovered that the unit used in these tests has a very narrow range of excess air levels within which it could operate. Below the minimum used in the tests (17% excess air), combustion was incomplete resulting in smoke formation. Above the maximum excess air used in the tests (53%) the fire would blow out the back of the combustion chamber and the system would automatically shut down. Furthermore, since this type of boiler is kept at a positive furnace pressure, a large change in excess air between minimum firing rate and maximum firing rate will not occur as it would in a negative pressure furnace.

The burner of the test unit is designed to fire on either gas or distillate oil. For normal operation, natural gas is fired. Therefore, the fuel oil firing system was available to be cleaned, adjusted, and used to fire test blends of liquid chemicals without interrupting normal operation of the boiler. The fuel oil system consists of a 1000-gal cylindrical tank, a pump with mechanical Teflon® seals, an atomizing air compressor, and a spray nozzle. The storage tank is plumbed to a nearby tank farm to permit filling the 1000-gal tank from long-term storage. Mixing is provided in the storage tank by a recycle loop from the boiler.

Test Fuel

To provide control of fuel composition and assure consistent purity in the materials burned for all test conditions, virgin chemicals were purchased and blended to simulate a hypothetical hazardous waste. Reagent grade carbon tetrachloride, technical grade monochlorobenzene, and technical trichloroethylene were carefully weighed to the desired amounts and added into the fuel tank. The tank was then topped off with nitration-grade toluene (>99% pure). Fuel was usually blended the evening before each test day so that the chemicals could mix overnight by recirculating through the fuel pump circuit. Table 1 shows the composition of the two test fuels fired in this program.

TABLE 1. AVERAGE POHCs COMPOSITION OF TEST FUEL

Fuel blend no.	Toluene (wt %)	Carbon tetra-chloride (wt %)	Trichloro-ethylene (wt %)	Chloro-benzene (wt %)
1	98	.5	1	.5
2	97	.5	2	.5

Test Matrix

Testing was conducted at six different boiler operating conditions. Table 2 summarizes the test matrix of fuel blend and boiler load/excess air (EA). Triplicate samples were collected with each test method at each test condition, except condition 6 for which only duplicate samples were collected.

TABLE 2. TEST MATRIX

Test condition no.	Fuel blend no.	Boiler conditions
1	1	half load
2	1	full load
3	2	half load
4	1	full load (high EA)
5	1	half load (high EA)
6	2	full load (load EA)

Procedures

The two volatile organic components of the fuel, carbon tetrachloride (CCl_4) and trichloroethylene (TCE) were sampled and analyzed according to the VOST protocol (1). Each test run consisted of three pairs (one Tenax®-GC and one Tenax®-GC/charcoal tube) except test 16 which consisted of six pairs and test 17 which consisted of four pairs. Sampling was conducted at 0.5 liters per minute (l/m). The volume sampled by each pair of tubes was 20 liters (1). VOST analytical results were subjected to the following acceptance criteria:

- Both surrogate compounds must have been detected.
- The fractional recovery of both surrogates must have been between 0.5 and 1.5.

OR

- The fractional recoveries of both surrogates must have been less than 5.0 and the two fractional recoveries must have agreed within 25%.

(recovery 1 divided by recovery 2 is between .75 and 1.25)

The semi-volatile organic compounds, toluene and monochlorobenzene (MCB), were sampled and analyzed by the MM5 procedure (2). Analysis of the resultant extracts was by GC/FID.

In addition to the VOST and MM5 sampling, the POHCs in the flue gas were determined by M23 (3). This method, shown schematically in Figure 1, employs integrated bag sampling followed by gas chromatography.

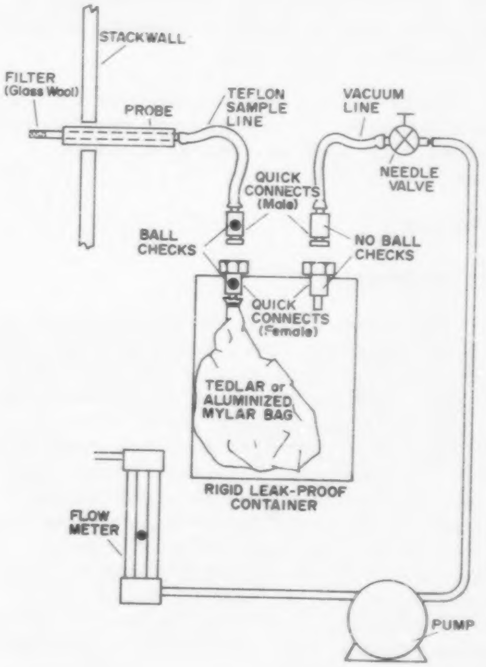
STACKWALL
FILTER (Glass Wool)
PROBE
TEFLON SAMPLE LINE
VACUUM LINE
QUICK CONNECTS (Male)
NEEDLE VALVE
BALL CHECKS
NO BALL CHECKS
QUICK CONNECTS (Female)
TEDLAR or ALUMINIZED MYLAR BAG
RIGID LEAK-PROOF CONTAINER
FLOW METER
PUMP

Figure 1. Schematic Diagram, Method 23 Sampling Equipment

The gas samples were collected in Tedlar® bags at a flow rate of 0.5 l/min over a 40-min interval simultaneously with the first leg of VOST sampling. Prior to testing, all Tedlar® bags were assembled, filled with ultra-pure nitrogen, leak checked, and tested by GC for background contamination. Toluene and chlorobenzene were analyzed by FID, while ECD was used for the remaining chlorinated POHCs. The sampling systems were also assembled and leak checked. Field sampling for POHCs consisted of two basic functions: preparation and analysis of calibration standards and flue gas sampling. Both functions were performed as described in M23. Spikes and replicate analyses were included in the flue gas analyses.

PROBLEMS ENCOUNTERED

VOST

An unusually large number of the VOST tubes were broken in shipment from the laboratory to the field. The breaks occurred at the Swaglok® fittings, indicating the fittings had been overtightened, had bottomed out on the tube, or the tube diameter was too large. Two tubes were broken on return to the laboratory, resulting in lost samples. There were problems with the GC/MS that resulted in two more lost samples, and there were four tube pairs that were lost by the laboratory. These lost samples combined with the data that were excluded because of poor surrogate recoveries resulted in a total of 21 tube pairs that were excluded out of a total of 55 tube pairs collected.

Modified Method 5

The analytical detection limit for MCB was four times higher than had been expected by the laboratory. As a result, for those runs where MCB was not detected, the maximum calculable DRE was less than 99.99%. There were 11 of 17 runs when MCB was not detected.

Method 23

Similar detection limit problems were encountered for MCB with the M23 procedure. The detection limit was only low enough to verify an average DRE of 95.64% when MCB was not detected, and MCB was not detected in any of the 18 test runs.

RESULTS

The boiler performed very well throughout the testing program. Only a few minor delays were encountered when steam production exceeded demand. Table 3 lists the average carbon monoxide (CO) and nitrogen oxides (NO_x) concentrations for each of the six test conditions. With the exception of condition 3 and 6 the CO results track boiler conditions as expected. For condition 3 and 6 the CO concentrations were lower than expected. These were the two runs with the highest fuel chlorine content, but it does not seem likely that the additional chlorine would have depressed the CO concentrations. The NO_x concentrations tracked boiler conditions as expected, although the NO_x concentration for condition 6 was lower than expected.

TABLE 3. CO AND NO_x RESULTS

Condition no.	Boiler load/EA (%)	Chlorinated Solvent (%)	CO (ppm)	NO_x (ppm)
1	half/38	2	108	172
5	half/50	2	89	130
3	half/31	3	10	158
2	full/38	2	142	82
4	full/41	2	86	75
6	full/17	3	20	84

Destruction Removal Efficiencies

DREs were calculated from measured fuel feed rates and compositions, flue gas flow rates, flue gas molecular weights, POHC flue gas concentrations, and POHC molecular weights.

Tables 4 and 5 show the calculated DREs obtained from the VOST and MM5 sampling, respectively. The values are the mass weighted averages for each boiler test condition. For toluene, carbon tetrachloride, and trichloroethylene the

DREs ranged from a low of 99.9976 to a high of 99.9999. The MCB results were lower, primarily because of the high analytical limit of detectability mentioned previously. The reported MCB DREs were calculated by inserting the minimum detectable quantity for the 11 runs where no MCB was detected. Therefore, the reported MCB DREs are lower than the actual DREs.

TABLE 4. DREs BY VOST

Condition no.	Boiler load/EA (%)	CCl_4 DRE (%)	TCE DRE (%)
1	half/38	99.9979	99.9999
3	half/31	99.9990	99.9995
5	half/50	99.9993	99.9976
2	full/38	99.9989	99.9998
4	full/41	99.9998	99.9999
6	full/17	99.9992	99.9996

TABLE 5. DREs BY VOST

Condition no.	Boiler load/EA (%)	Toluene DRE (%)	MCB DRE (%)
1	half/38	99.9997	99.952
3	half/31	99.9992	99.978
5	half/50	99.9991	99.972
2	full/38	99.9991	99.946
4	full/41	99.9994	99.948
6	full/17	99.9991	99.973

For the M23 results, there were only four test runs in which POHCs were found in the flue gases. In the cases where no POHCs were detected, the analytical detection limit was used to calculate the DRE. Therefore, the actual DREs occurring in the boiler were at least as great or greater than the calculated DREs. With the exception of MCB, the M23 analytical procedures were sensitive enough to substantiate at least 99.99% DRE. Because most of the DREs were based on detection limits, the individual values by test condition are not given. Instead, Table 6 shows the number of runs for which DREs greater than and less than 99.99% were verified.

TABLE 6. DREs BY M23

POHC	No. of cases DRE >99.99%	No. of cases DRE >99.99%
Toluene	17	1(a)
CCl_4	17	0
TCE	12	3(b)
MCB	0	18

(a) measured DRE ÷ 99.98
(b) average measured DRE = 99.46

Table 6 illustrates the average DREs calculated for each of the four POHCs by the M23 procedure. The DREs reported in Table 6 illustrate that the EPA Method 23, coupled with GC/FID-ECD analysis, was sufficient to subtantiate DREs of at least "four nines" occurring in the test boiler for toluene, CCl_4, and TCE. Because of the low instrument sensitivity to MCB, however, this method could not provide adequate sensitivity for DRE measurement of this POHC under the given test conditions. The best DRE calculable for MCB under these conditions averaged 95.64.

Methods Comparison

A direct comparison of the POHC concentrations measured by the various methods is not possible because only four of the 72 determinations by M23 yielded detectable POHC quantities. It is possible, however, to compare the DREs obtained with the three methods as shown in Table 7. The test results for all six test conditions was combined to give a mass weighted average DRE for each POHC. The VOST and MM5 test procedures yielded higher DRE values for each POHC than did the M23 procedure. The reason that the DRE values are higher for VOST and MM5 than for M23 is because VOST and MM5 had lower limits of detectability. With the exception of MCB, VOST and MM5 were able to measure actual flue gas concentrations and thus actual DREs could be calculated.

Method 23 could only provide information that the DRE was at least as great as the calculated value, based on the higher limit of detectability inherent with M23.

TABLE 7. DREs COMPARISON

Compound	DRE by VOST or MM5	DRE by Method 23
Toluene	99.999	>99.998
CCl_4	99.999	>99.954
TCE	99.999	>99.995
MCB	>99.961	>95.642

It is important to emphasize that the M23 DREs reported in Table 7 are more a reflection of limitations in analytical methods sensitivity than of the ability of the test boiler to destroy or remove the test POHCs. The test boiler likely destroyed or removed a larger percentage of the input POHC load than is reported.

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PARAMETRIC EXPERIMENTATION WITH A PILOT-SCALE BOILER BURNING HAZARDOUS COMPOUNDS

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ABSTRACT

Thermal destruction of wastes by direct incineration or by cofiring with conventional fuels in boilers, furnaces, or kilns is one of the most effective methods currently available for disposal of hazardous organic material. While direct incineration of hazardous wastes is regulated by Part 264 of the Resource Conservation and Recovery Act (RCRA) as adopted in January 1981, boiler cofiring is currently exempt from RCRA provisions. However, the potential for boiler cofiring regulations has been evaluated by the Environmental Protection Agency (EPA) and they are now in the process of preparing regulatory positions in drafting regulations for promulgation. To support this effort, EPA's Incineration Research Branch (IRB) in conjunction with the Office of Solid Waste is conducting research and development programs on incineration effectiveness and regulatory impacts.

The global purpose of this study was to gather data to aid the EPA in selecting a strategy or set of strategies for regulating the combustion of hazardous wastes in boilers. The specific objectives were twofold: to identify which of several boiler operational parameters have a major impact on boiler destruction and removal efficiency; and, to evaluate and if practical, establish a mathematical model for predicting an upper limit on the amount of cofired waste that could be emitted. In particular, those parameters that could be easily changed by an operator or might represent major differences between boiler types were studied. A secondary objective of the study was to gain sufficient information to allow judgements of what particular parameters to monitor closely during full-scale testing.

GENERAL APPROACH AND TEST MATRIX

The experimental goals of the program, in sequence, were to:

- Determine the furnace operating parameters which affect the furnace three-dimensional time-temperature environment
- Quantify these effects
- Identify the relationships between operating parameters, time-temperature history, and destruction of hazardous waste components in the fuel

The test plan divided the tests into three subsets: a baseline study burning only distillate oil, a single compound study of one hazardous waste compound cofired with distillate oil, and a multiple compound study burning more than one compound simultaneously. The baseline study was designed to define the thermal environment within the facility under the various operating conditions of choice, to define the magnitude of the effects of changes in variables on the thermal environment, and to demonstrate the ability of a simulation to predict the thermal environment resulting from a specific set of variable settings. The single compound studies had two goals: to define the magnitude of variable effects on destruction efficiency; and to define the effects of cofiring wastes on the expected thermal environment. The final, multiple compound studies were to determine the destruction efficiencies of several compounds with known thermal environments. Chlorinated wastes were selected for sensitivity and ease of analysis. Chlorobenzene was selected for the single compound tests because of its high heat content, compatibility with distillate oil, and simple structure. For the multiple compound tests chlorobenzene was fired with carbon tetrachloride, chloroform, methylene chloride, and dichloroethane.

Within each task a set of independent variables were identified that are relevant to the operation of incinerators and boilers.

Table 1 shows the test matrix of nominal operating conditions used in the program. Firing rate and stoichiometry parameter values are listed at nominal conditions based on analysis of the pure distillate oil fuel. As shown, two nominal firing rates (0.2 and 0.38 megawatts) and three nominal stoichiometries (10, 25, and 50 percent excess air) were used.

The highest concentration of waste to fuel was achieved with chlorobenzene (10 percent v/v). Other materials were injected at levels of approximately 1.5 to 3.5 percent (v/v).

A total of 40 tests were run generating 99 individual data points. Fourteen firing conditions were studied and the destruction and removal efficiency relative to four compounds was examined. A computer simulation was prepared that predicted the thermal profile within 25°C and the destruction and removal efficiency within two orders of magnitude.

FACILITY DESCRIPTION

All tests were performed in the Acurex Pilot-Scale Furnace. The furnace has a single burner, front wall fired, into a horizontally oriented firebox. The premixed fuel oil/waste mixture is pumped out of drums through a pressure-atomizing nozzle and stabilized at the front wall. The fuel flow is monitored by rotometer. Combustion air is preheated and injected in the annular region around the fuel delivery tube. The IFRF/Acurex burner design allows swirl adjustment by rotating swirl blocks. Air flow is monitored by hot wire anemometer.

The walls of the radiant section are refractory lined with optionally mounted waterwalls. Ports along the top and sides of the furnace accommodate ceramic type R thermocouple probes for gas temperature profiles. Type K probes are

TABLE 1. TEST MATRIX OF VARIABLES AND NOMINAL VALUES

Variable	Values
Firing rate (load)	0.23, 0.35 ± 0.03 megawatts (0.8, 1.2 ± 0.10 million Btu/hr)
Flame shape (swirl)	7.5, 5.0, 2.0
Excess air rate (stoichiometry)	10, 25, 50 percent, ±2 percent
Waste to fuel ratio	10, 3, 1.5 percent
Waterwall area	0, 8 percent
Compounds	4

embedded in the refractory for wall temperature determinations. Thermocouples are also placed at the manifold inlet to and the outlet of each cooling panel, and to and from the burner quarl. Cooling fluid flow measurements are by rotometer. Downstream of the convective a stainless steel probe extracts gas samples for continuous emissions analysis. Electro-optical analyses are used to define levels of CO, CO_2, O_2, NO_x, and total unburnt hydrocarbon (THC). Samples for the Volatile Organics Sampling Train (VOST) are extracted with a stainless steel probe from the end of an 8-in. diameter 15-ft long duct. The gases are then exhausted to a 45-ft high stack.

RESULTS AND DISCUSSION

Table 2 provides a complete summary of the program results. The roman numeral in the first column is an identifier for the run condition. The run condition is summarized in the second column. The first item in parentheses is the nominal firing rate in million Btu/hr. The second and third items are the percent excess air and the swirl setting, respectively. The finalitem is the percent of the radiative section surface area covered by water walls. The number in the compound columns represent the average penetration value, C/C_0, (mass of waste out per unit time/mass rate of waste in), the value of one standard deviation, and (in parentheses) the number of data points. The relationship to DRE is: $DRE = 1-C/C_0$. The effects of the various firing conditions of DRE's are discussed in the following sections. A semiquantitative summary on the variable effects is given in Table 3. These values are rough estimates of the difference between either temperature or DRE for two runs where only the specified parameter was

TABLE 2. AVERAGE FRACTIONAL BREAKTHROUGH C/C_0 FOR EACH WASTE AND FIRING CONDITION

Condition		Chlorobenzene*,†	Carbon tetrachloride	Chloroform	1,2 Dichloroethane
I‡	(0.8, 10, 7.5, 8)	$1.4 \pm 0.1 \times 10^{-4}$ (4)	$1.6 \pm 0.2 \times 10^{-4}$ (2)	$1.6 \pm 0.2 \times 10^{-5}$ (3)	$5 \pm 2 \times 10^{-6}$ (3)
Ia§	(0.8, 10, 7.5, 0)	4.2×10^{-6} (1)	--‖	--	--
II	(0.8, 25, 7.5, 8)	$1.4 \pm 0.3 \times 10^{-5}$ (4)	$5 \pm 3 \times 10^{-5}$ (5)	$2.6 \pm 2 \times 10^{-5}$ (5)	$1 \pm 0.5 \times 10^{-6}$ (2)
IIa	(0.8, 25, 7.5, 0)	$4 \pm 3 \times 10^{-7}$ (6)	--	--	--
III	(0.8, 50, 7.5, 8)	$8.9 \pm 6 \times 10^{-5}$ (5)	2.1×10^{-4} (1)	$2.0 \pm 0.8 \times 10^{-5}$ (3)	$1 \pm 0.2 \times 10^{-6}$ (3)
IIIa	(0.8, 50, 7.5, 0)	$2.5 \pm 2 \times 10^{-7}$ (3)	--	--	--
IV	(1.2, 10, 7.5, 8)	$6 \pm 8 \times 10^{-5}$ (5)	$1.2 \pm 0.3 \times 10^{-4}$ (2)	$3.2 \pm 0.5 \times 10^{-5}$ (3)	--
IVa	(1.2, 10, 7.5, 0)	$2.2 \pm 0.5 \times 10^{-7}$ (3)	--	--	--
V	(1.2, 25, 7.5, 8)	$4.5 \pm 2 \times 10^{-6}$ (5)	$2.5 \pm 1 \times 10^{-5}$ (2)	$8.8 \pm 2 \times 10^{-5}$ (3)	--
Va	(1.2, 25, 7.5, 0)	$0.5 \pm 0.3 \times 10^{-7}$ (3)	--	--	--
VI	(1.2, 50, 7.5, 8)	$5.5 \pm 2 \times 10^{-5}$ (4)	$7.9 \pm 6 \times 10^{-5}$ (3)	$1.1 \pm 0.02 \times 10^{-4}$ (2)	$8 \pm 4 \times 10^{-6}$ (2)
VIa	(1.2, 50, 7.5, 0)	$3.4 \pm 0.7 \times 10^{-7}$ (3)	--	--	--
VII	(0.8, 25, 5.0, 8)	--	$6.3 \pm 3 \times 10^{-5}$ (3)	--	--
IX	(1.2, 25, 5.0, 8)	$2.0 \pm 0.5 \times 10^{-6}$ (3)	$1.5 \pm 0.3 \times 10^{-4}$ (3)	--	--

* ± represents 1 standard deviation from average.

† ( ) indicates number of valid data points.

‡ Firing rate in million Btu/hr, percent excess air, swirl, percent waterwall.

§ Run conditions suffixed with an "a" are without waterwalls. All other conditions are with waterwalls in place.

‖ Not tested under that condition.

TABLE 3. SEMIQUANTITATIVE ESTIMATION OF THE EFFECTS OF THE INDEPENDENT VARIABLES ON TEMPERATURE PROFILE AND DRE

Variable	Range of Temperature Changes °C	(±°F)	Range of DRE Changes (Factor)*
Waterwalls	275	(500)	100
Excess air rate	165	(300)	10
Firing rate	110	(200)	3
Burner swirl	30	(50)	1
Compound	30	(50)	20

*C/C_0 is mass rate of waste out divided by mass rate of waste in.

varied. For example, a change in firing rate between 0.8 million Btu/hr and 1.2 million Btu/hr changed the temperature profile by about 110°C (200°F). The corresponding change in DRE was about a factor of three.

Thermal profiles were presented in detail in a previous paper (1) and will be discussed only incidentally to DRE discussions. The temperature profiles clearly show a thermal boundary layer within four inches of the furnace wall. This boundary layer is significant, since it represents greter than 40 percent of the volume or thermal environment of the furnace. Because temperature and velocity are the dominant factors in volume flowrate and destruction, this zone will be significant when considering destruction efficiencies in this furnace.

Effect of Waterwalls on Thermal Environments and DRE's

Addition of waterwall panels replaced about 8 percent of the refractory surface area but extracted 50 to 60 percent of the heat input. With the waterwalls in place the thermal environment of the first six feet of the firebox was comparable to a D-type packaged watertube boiler. However, the pilot-scale waterwall surface temperature is much lower than for industrial boilers (600° to 800°F). The effect will be to lower DRE in the pilot unit with respect to an industial boiler through wall quenching. This is offset by the larger industrial boiler waterwall surface area (>50 percent) compared to the pilot unit.

Waterwalls have a dominant effect on DRE. This is shown in Table 4. For chlorobenzene DRE varied over two orders of magnitude with the introduction of wall cooling. Qualitatively, this was to be expected since the waterwalls decreased the corresponding temperature profiles 220 to 280°C (400° to 500°F). Not surprisingly, the magnitude of the effect is within the range predicted by theory. Using the Arrenius expression for a rate constant, $k = A_{exp}\ (-E_a/RT)$, and algebraically manipulating the kinetic expressions to present the ratio of breakthrough fractions for a given waste under two different temperatures, one obtains

$$C_1/C_2 = \exp\ [E_a\ (T_1 - T_2)/RT_1T_2]$$

C_1 and C_2 are the breakthrough quantities at two different run temperatures (assuming the same feedrate in), E_a is the empirical pseudo first order energy of activation for the disappearance of the waste, R is the appropriate gas constant, and T_1 and T_2 are the effective temperatures. Using effective temperatures of 1,100 and 1,380K, an activation energy of 50 kilocalories per gram mole, and a gas constant of 1.982 calories per gram mole °K, the calculated ratio of breakthrough quantities is 100.

TABLE 4. AVERAGE MEASURED PENETRATION C/C_0 OF CHLOROBENZENE

Condition	With Water Walls (x 10^5)		Without Water Walls (x10^7)	
(0.8,10,7.5)	14 ± 1	(4)	40	(1)
(0.8,25,7.5)	1.4 ± 3	(4)	4 ± 3	(6)
(0.8,50,7.5)	8.9 ± 6	(5)	3 ± 2	(3)
(1.2,10,7.5)	6 ± 8	(5)	2 ± 0.5	(3)
(1.2,25,7.5)	0.5 ± 0.2	(5)	0.5 ± 0.3	(3)
(1.2,50,7.5)	5.5 ± 2	(4)	3 ± 0.7	(3)

Effect of Excess Air on Temperature Profiles

The effects of excess air on temperature profiles followed expectation. A comparison of Figures 1 and 2 shows effects of excess air on centerline axial temperature profiles for different firing rates. An alternate demonstration is given in Figure 3. Here, radial temperature profiles at two positions are shown for three excess air levels at a nominal 0.8 million Btu/hr firing rate. All three conditions are without waterwalls. On the centerline, gas temperatures vary as much as 140°C (250°F) at cross section C-3 (approximately 80 in. from the burner face) but only approximately 40°C (70°F) at position E-2 (114 in. from the face). The equivalent temperature difference at the higher firing rate of 1.2 million Btu/hr are on the order of 80°C and 25°C (150° and 50°)F), respectively. The lower difference at the higher firing rate is caused by radiative effects from the hotter flame zone radiating into the cooler postflame zone.

Qualitatively these excess air results will have opposing effects on destruction efficiencies. At the higher excess air level the increased oxygen content will promote destruction while the decreased residence time and temperature will suppress destruction. In fact, there appears to be a peak destruction efficiency between excess air rates of 10 and 50 percent. This is shown graphically in Figure 4.

Effect of Swirl on Temperature and DRE

From the observed temperature profiles, the effect of increased swirl is to increase the temperature gradient. However, the temperature changes only about 15°C (25°F) at the centerline. This is comparable to the measured temperature variance between runs (see Table 2), and is probably not significant. There may be a significant variation in DRE with swirl, but the data is difficult to interpret. A significant difference is seen only in the long, thin flame (swirl setting 2.0), but it is in the opposite direction for chlorobenzene and carbon tetrachloride.

Products of Incomplete Combustion

In order to maximize the number of variable data points, the analytical design for this program was simplified by not performing GC/MS analyses. This reduced the ability to identify and quantitate PIC's. Because the program was not directed toward PIC's, much raw data (such as the numerous chromatographic strips) that contains PIC information has not been reduced. However, even with limited examination of the data some important information is available. For example, in every run methylene chloride was observed at levels equal to or greater than the POHC of interest, even when it was not present as a POHC in the waste (Figure 5 displays typical chromatograms from the analysis). Although some of this methylene chloride can be attributed to contamination, the levels were consistently higher than corresponding blank values. Peaks in the retention time range for methylene chloride were routinely off scale. Several other chlorinated organics not fired in the fuel have been identified as being in the emissions of one or chlorinated organics not fired in the fuel have been identified as being in the emissions of one or more runs. These include such species as trichloroethylene, the dichloroethylenes, chloroform, and possibly chloromethane. An example is given in the summary Table 5. The significance of this finding is the following -- although DRE's for both POHC's (chlorobenzene and carbon tetrachloride) are greater than 99.99 percent, the DRE of total chlorinated organics as fired is only 99.985 percent.

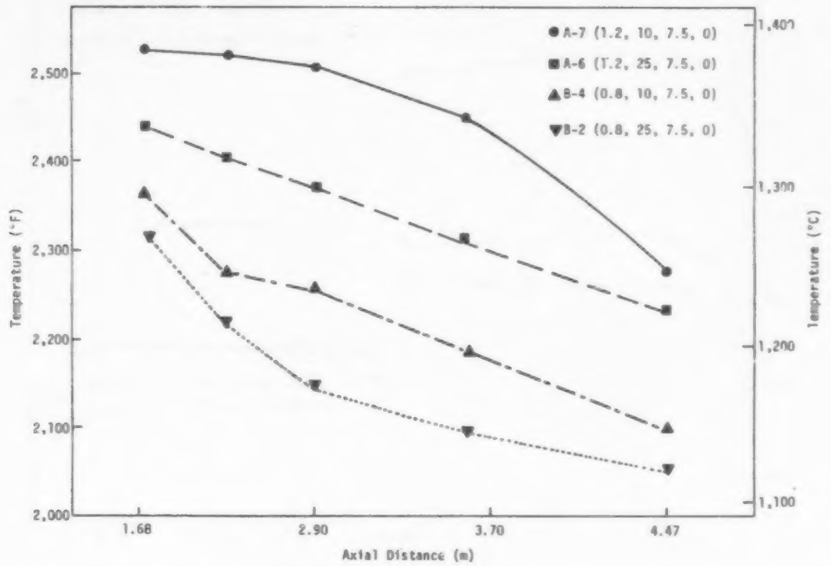


Figure 1. Centerline Axial Temperature Profiles for Four Firing Conditions Without Waterwalls.

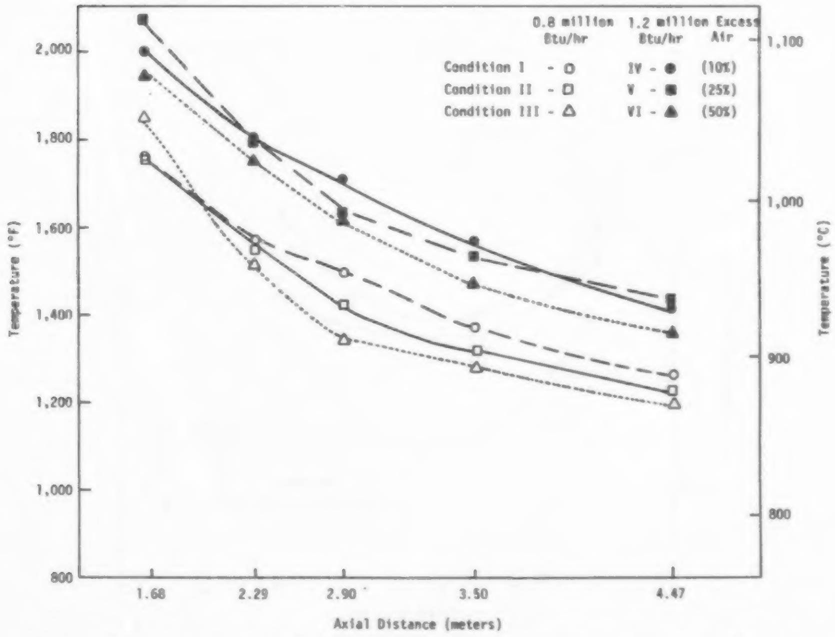


Figure 2. Centerline Axial Temperature Profiles for Six Firing Conditions with Waterwalls.

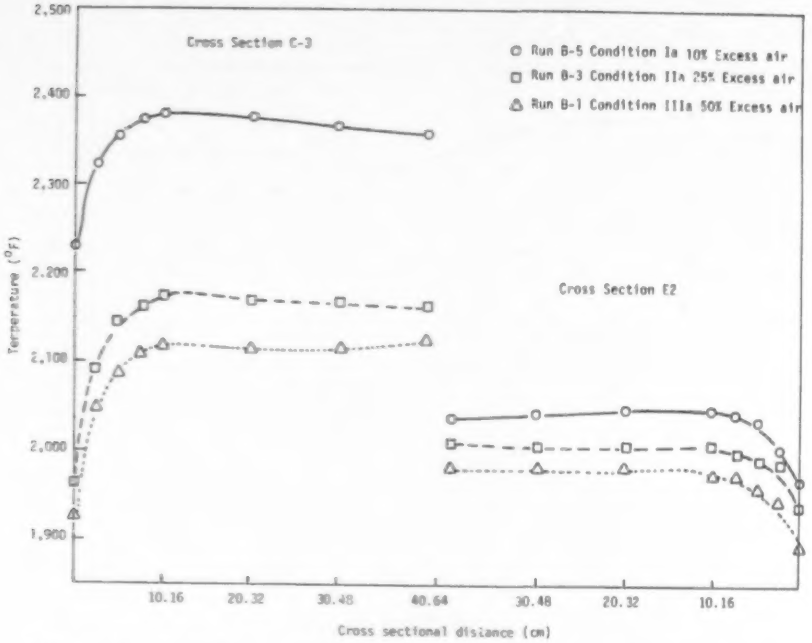


Figure 3. Effects of Excess Air on Temperature for Three Firing Conditions Without Waterwalls. Normal Firing Rate is 0.8 million Btu/hr.

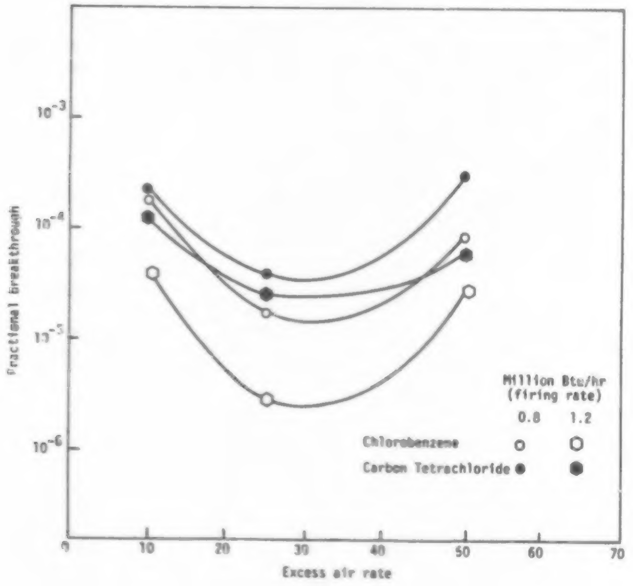


Figure 4. Effect of Excess Air on Fractional Breakthrough for Carbon Tetrachloride and Chlorobenzene.

TABLE 5. SUMMARY OF RUN C-7

	Chlorobenzene	Carbon tetrachloride	Chloroform*	Subtotal†	Other‡	Total§
Mass flow in‖	17.34	9.72	0	27.05	0	27.05
Mass flow out**	1.48×10^{-5}	8.32×10^{-4}	1.22×10^{-3}	2.06×10^{-3}	2×10^{-3}	4×10^{-3}
Out/in	8.54×10^{-7}	8.56×10^{-5}	N/A	7.62×10^{-5}	N/A	1.48×10^{-4}
Average DRE	99.9999 ±0.00016††	99.9914 ±0.0035	N/A	99.9924 ±0.004	N/A	99.985 ±0.020

* Major identified PIC.

† Includes POHC's plus chloroform.

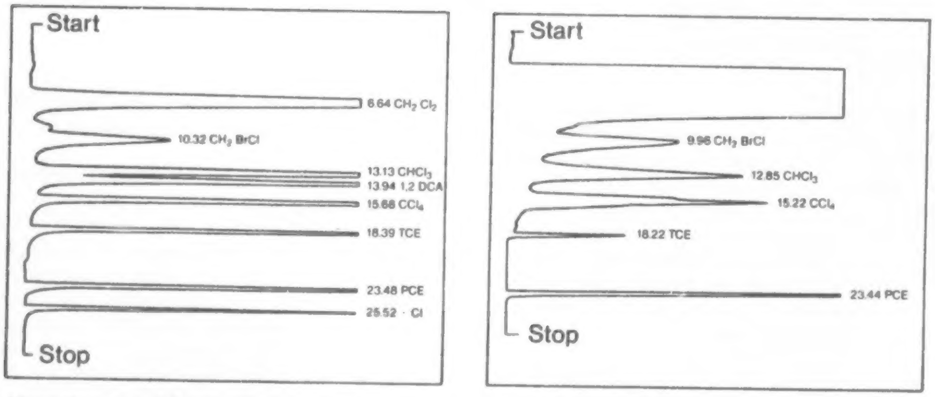
‡ Estimate of unidentified and/or unquantified PIC's.

§ Estimate of total chlorinated organic species.

‖ Estimate of total g/min.

** Average of three samples (g/min).

†† Two standard deviation.



Standard 1,000 ng each on blank trap

Sample run C-7B carbon tetrachloride

Figure 5. Typical Chromatograms Demonstrating Presence of PIC's.

PRODUCTS OF INCOMPLETE COMBUSTION FROM HAZARDOUS WASTE INCINERATORS

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ABSTRACT

The Environmental Protection Agency (EPA) is preparing a Regulatory Impact Analysis (RIA) of hazardous waste incineration. Midwest Research Institute (MRI) provided input data to the RIA from tests conducted at eight incineration facilities. This paper presents information gathered during these tests related to products of incomplete combustion (PICs). PICs were defined as any hazardous organic constituent detected in the stack gas but not present in the waste feed at a concentration of 100 μg/g or higher. Benzene and chloroform were the compounds found most often among approximately 30 identified PICs. PIC emissions were comparable to principal organic hazardous constituents (POHC) emissions in concentration and total mass output. Three mechanisms are proposed to account for the presence of PICs: (a) POHCs in the waste feed below detection limits, subject to low destruction and removal efficiency (DRE), and therefore detected in the stack gas; (b) introduction into the system from some source other than the waste feed (e.g., auxiliary fuel, in-leak air, scrubber water); and (c) actual PICs (compounds occurring as a result of combustion reactions).

INTRODUCTION

Incineration is a popular option for ultimate disposal of combustible hazardous wastes. While incineration provides a high degree of destruction for compounds in the waste feed streams, questions have been raised about possible byproducts of combustion reactions. This paper addresses some of these concerns based on results of tests at full-scale operating incinerators.

Midwest Research Institute (MRI) performed a series of tests at operating hazardous waste incineration facilities and analyzed the collected samples for products of incomplete combustion (PICs). These tests were performed as part of technical support to EPA's preparation of a regulatory impact analysis (RIA) for hazardous waste incinerators.

Prior to this study by MRI, the accumulated data base on products of incomplete combustion of Appendix VIII compounds, principal organic hazardous constituents (POHCs), was limited primarily to laboratory scale studies. In those studies, certain specific compounds were thermally destroyed in high concentrations to test for possible PICs. Compounds tested include kepone[1] and polychlorinated biphenyls.[2] These studies are illuminating for specific cases, but the data base for PICs from combustion of the complex matrices of organic constituents which currently are being fed to hazardous waste incinerators was virtually nonexistent before MRI's study.

This paper first describes briefly the MRI study and identifies some of the limitations of the data base. Then, results of the tests conducted are discussed in terms of three possible mechanisms to explain the presence of PICs in the stack gas, and the relative contribution of each mechanism. The conclusion section contains some general observations. This paper is intended to be an overview of the PIC phenomenon. It does not provide final definition of mechanisms for PIC formation.

MRI STUDY OF HAZARDOUS WASTE INCINERATION FACILITIES

PICs were defined for this study as any Appendix VIII compound detected in the stack gas which was not present in the waste feed in concentrations greater than 100 μg/g. The study included measurement of PICs at eight full-scale operating incinerators with a variety of key design and operating parameters and waste feed characteristics. Each incinerator had a liquid injection burner, and some facilities also included a rotary kiln or hearth. Three incinerators had no air pollution control devices. The remaining five had wet scrubbers for HCl control, and four of these had other particulate control devices.

Combustion chamber designs were varied. Several facilities had multiple combustion chambers. The incinerators ranged in waste feed capacity from 50 to 6,000 kg/hr (110 to 13,000 lb/hr), with corresponding heat inputs from 1 to 78 GJ/hr (1 to 74 million Btu/hr). Operating conditions for three key parameters exhibited wide ranges: combustion temperature, 820° to 1450°C (1400° to 2650°F); residence times, 0.07 to 6.5 sec; and percent excess air, 60 to 130%.

The facilities included some examples of incineration of specific process wastes generated onsite as well as varied mixtures of wastes disposed offsite. The wastes fired at different facilities varied also with respect to waste type (liquid, solid, and gas), heating value, chloride concentration, and ash and moisture content. The organic liquids and many of the solids had a heating value high enough to sustain combustion without auxiliary fuel. Percentages of chloride ranged up to 25%, the highest values occurring for organic liquids. Ash values ranged up to 9% for organic liquids and 29% for solids. Water content ranged up to 50% for organic liquid and solid wastes, and to nearly 100% for aqueous wastes.

Samples were collected of all inflow and outflow streams at the incineration facilities. All samples were analyzed for Appendix VIII constituents by gas chromatography/mass spectrometry. Lower detection limits for compounds in the waste feed ranged from 1 μg/g up to 100 μg/g, depending on the variety and complexity of the sample matrix. The sampling and analysis procedures used were capable of quantifying a wide variety of compounds present in the stack gas with lower detection limits of 1-2 ng/L.

Certain compounds which are suspected of being PICs were not amenable to measurement by the methods used in these tests, e.g., formaldehyde and phosgene. Also, at seven of the eight facilities, carbon tetrachloride and trichloroethylene were present in the waste feed, limiting their identification as common PICs.

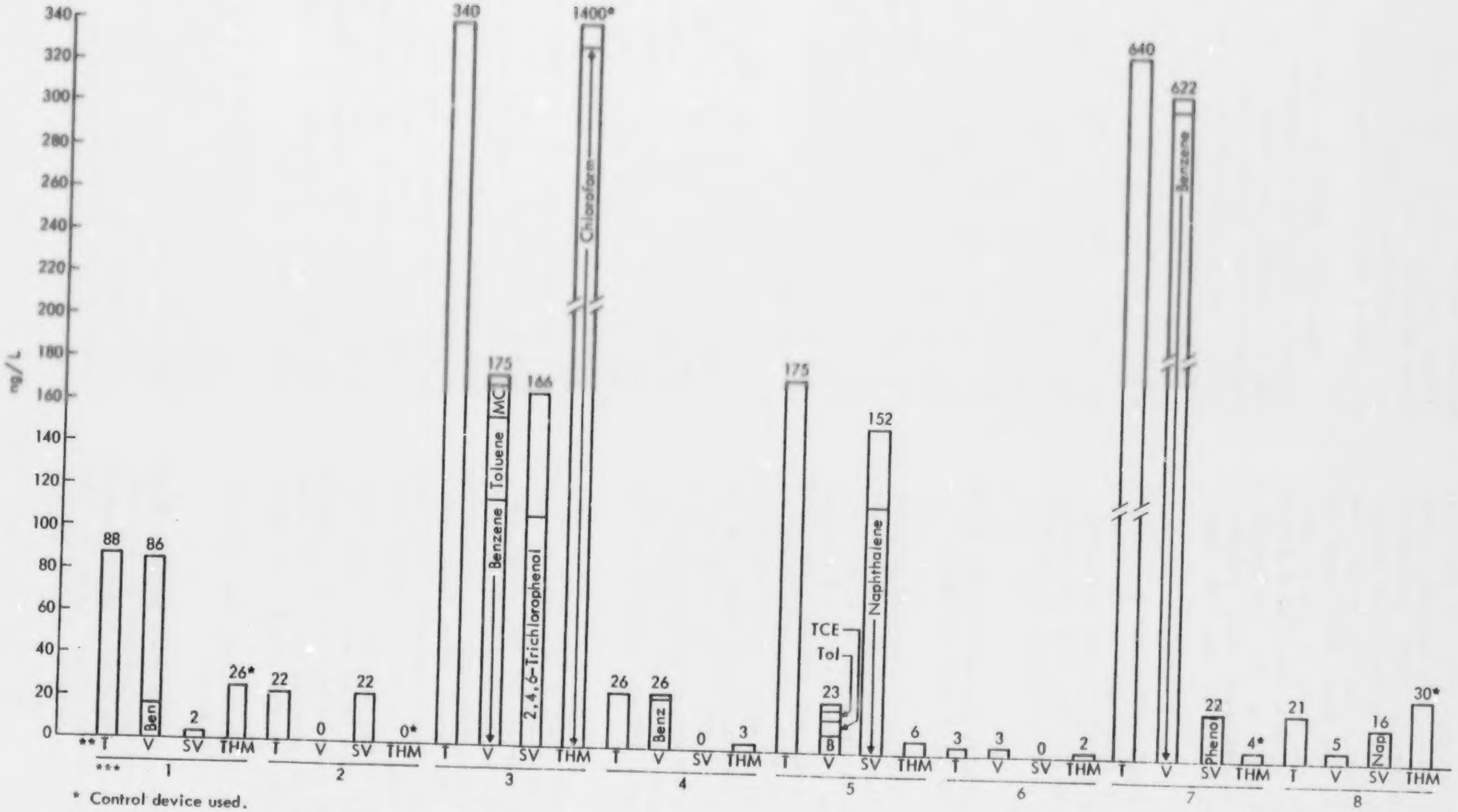
PRESENCE OF PICs IN THE STACK GAS--AN OVERVIEW

Twenty-nine compounds were classified as PICs from the eight incinerator tests. These compounds are shown in Table 1 along with the number of sites where they were detected as PICs and the range of concentrations measured in the stack effluents. Figure 1 shows an alternate display of the data categorized as volatiles, semivolatiles, and trihalomethanes (THMs). The total concentrations of all PICs, and of the three categories of PICs are shown for each plant. THMs are not included in the totals because they may have originated in the liquid influent to the control systems at some plants.

Total stack output of Appendix VIII compounds for the eight plants is shown

TABLE 1. PICs FOUND IN STACK EFFLUENTS

PIC	Number of sites	Concentrations (ng/L)
Benzene	6	12-670
Chloroform	5	1-1,330
Bromodichloromethane	4	3-32
Dibromochloromethane	4	1-12
Naphthalene	3	5-100
Bromoform	3	0.2-24
Chlorobenzene	3	1-10
Tetrachloroethylene	3	0.1-2.5
1,1,1-Trichloroethane	3	0.1-1.5
Toluene	2	2-75
o-Nitrophenol	2	25-50
Methylene chloride	2	2-27
Phenol	2	4-22
2,4,6-Trichlorophenol	1	110
Carbon disulfide	1	32
o-Chlorophenol	1	2-22
2,4 Dimethyl phenol	1	1-21
Methylene bromide	1	18
Bromochloromethane	1	14
Trichlorobenzene	1	7
Hexachlorobenzene	1	7
Diethyl phthalate	1	7
Pentachlorophenol	1	6
Dichlorobenzene	1	2-4
Chloromethane	1	3
Methyl ethyl ketone	1	3
Bromomethane	1	1
Pyrene	1	1
Fluoranthene	1	1



* Control device used.

** T = Total, V = Volatile, SV = Semivolatile, THM = Trihalomethanes - chloroform, bromoform, bromodichloromethane, dibromochloromethane (not included in other totals).

*** Numbers 1-8 identify the plants.

Figure 1. Summary of PIC Concentrations

as a comparison between PICs and POHCs in Figure 2. In general, PIC concentrations are slightly higher than POHC concentrations, although this ratio varies widely from plant to plant. The PIC output was also compared to the total POHC input in the waste feed. As Table 2 shows, only one of the eight plants exceeded 0.01% of POHC input, leading to the conclusion that the PIC output rate only infrequently exceeds 0.01% of the POHC input rate.

Three possible mechanisms to explain the presence of compounds in the stack gas classified as PICs were assessed. These mechanisms and the relative contribution of each are discussed in the following sections.

Compounds Originally Present in the Waste Feed Below 100 µg/g with Low DRE

For this study, a compound present in the waste feed below 100 µg/g but detected in the stack would be classified as a PIC. The approximate stack concentration for a compound present just below 100 µg/g, if it were subject to a DRE of 99.9%, would be 10 ng/L. Since this concentration is substantially above the detection limit of the stack sampling method, the compound is identified as a PIC. Data gathered on the program confirmed that this situation might be reasonably expected.

In certain cases, the waste feed samples were relatively "clean" and detection limits were on the order of 1 µg/g. These waste feed samples frequently contained compounds at concentrations below 100 µg/g. When DREs were calculated for these compounds, they generally fell below 99.9%. Although this mechanism would not account for a large percentage of the total mass output of Appendix VIII compounds, it could explain the presence of several of the PIC compounds detected in the stack effluents.

Compounds Introduced from Some Source Other Than Waste Feed

PIC compounds may also be introduced to the incineration process by streams other than the waste feed. Three sources are: (1) scrubbing liquid used in control devices; (2) inleak of ambient air through spaces in ductwork; and (3) auxiliary fuel streams. Instances of all three possible sources of introduction to the incineration process occurred during the course of the testing program.

Municipal water is often used as makeup to scrubbers. Appendix VIII compounds commonly are found in measurable concentrations in municipal water supplies. These compounds are primarily the THMs mentioned earlier, and they are introduced into the water via chlorination. The THMs are in low concentrations in the water inflow streams, but can be stripped out of the water with high efficiency by the hot stack gases. In a number of cases the scrubber water effluents contained substantially less of these organic compounds than did the makeup water. This phenomenon could account for the presence of THMs which appear as PICs in the stack effluent of plants with wet control devices using chlorinated makeup water. In addition to THMs contributed by treated water supplies, other trace organics can sometimes be found in well water or lagoon water used as makeup to scrubbers.

Typically, a plant exhibited a scrubber makeup flow rate of 70 L/min (18 gpm) and a stack flow rate of 100 Nm^3/min (3,500 dscfm). THMs were measured in makeup water at concentrations of 100 µg/L for chloroform and 10 µg/L each for bromodichloromethane, dibromochloromethane, and bromoform. The scrubber water was stripped clean of all THMs (the effluent contained $<$ 1 µg/L of all compounds). This stripping resulted in a contribution to the stack effluent of 0.007 g/min (70 ng/L) for chloroform and 0.0007 g/min (7 ng/L) for each of the other THMs. These concentrations were easily detectable by the sampling methods used. In one case, well water used for a quench makeup was found to contain four Appendix VIII compounds in quantities greater than 100 µg/L.

A second possible source of Appendix VIII compounds in the stack effluent is ambient air that may enter the negative pressure system through spaces in ductwork or other openings downstream from the combustion chamber. Heat balance calculations performed upon the eight incinerators indicated that from 0 to 50%

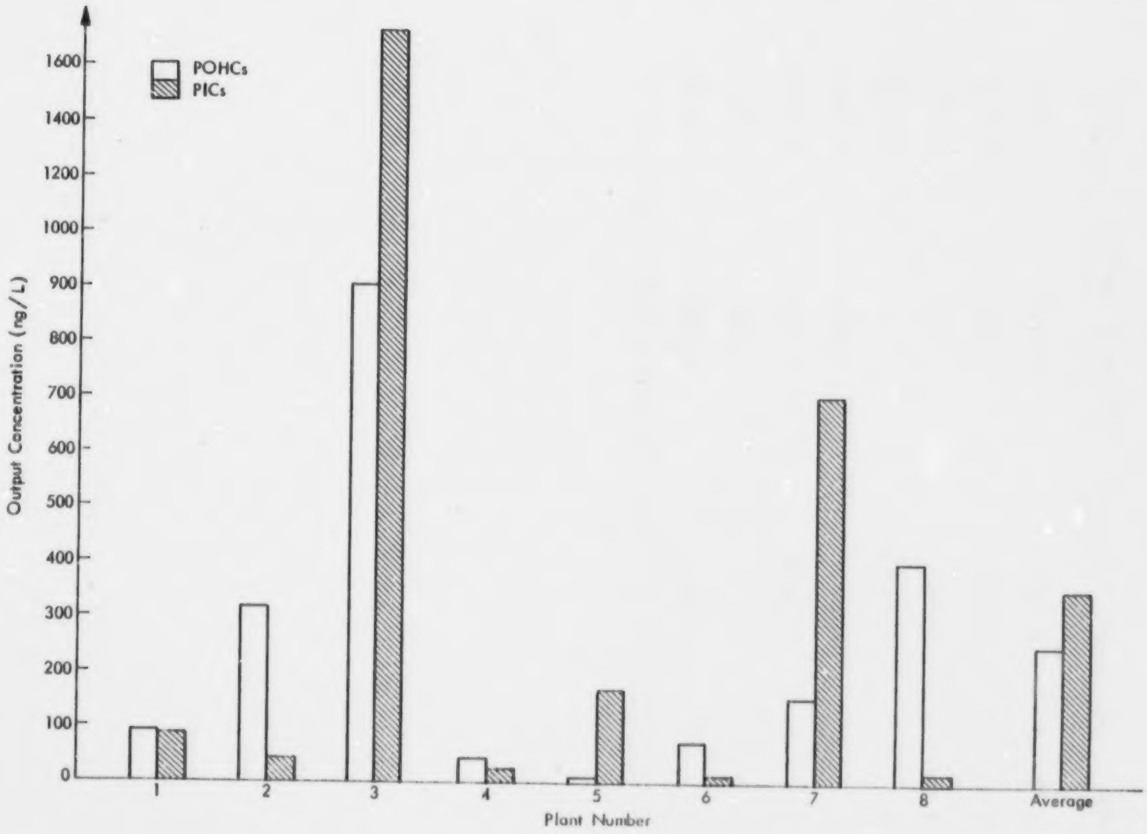


Figure 2. POHC Output Compared to PIC Output

TABLE 2. CALCULATED VALUES FOR PIC EMISSIONS AS A PERCENTAGE OF POHC INPUT

Calculated values for PIC emissions as a percentage of POHC input:

$$\% = \frac{\text{PIC output (g/min)}}{\text{POHC input (g/min)}} \times 100$$

Plant	PIC output (g/min)	POHC input (g/min)	%
1	0.090	9,800	0.00092
2	0.0046	100	0.0044
3	0.092	780	0.012
4	0.00062	27	0.00023
5	0.011	1,200	0.00091
6	0.00090	310	0.00039
7	0.26	8,300	0.0031
8	0.0076	1,200	0.00061

of the measured stack flow rate might have entered the system downstream from the combustion chamber. It is not unusual for ambient air to contain higher concentrations of some Appendix VIII compounds than the concentrations measured in the incinerator stack.[3] The ambient air concentrations may be higher in areas of a facility where hazardous wastes are handled.

Ambient air samples collected at one facility contained measurable concentrations (between 2 and 30 ng/L) of eight Appendix VIII compounds, as shown in Table 3. The inleak rate at this plant was calculated to be 25% of the total stack flow. This inleak rate was used to calculate the figures shown for contribution to stack gas concentrations. All of these compounds were detected at low levels in the stack, so this source is not suspected of contributing a large mass flow rate of compounds; but it still can result in the identification of additional compounds as PICs.

A third potential source of Appendix VIII compounds is the auxiliary fuel stream, which is not usually classified as a waste feed. Uncombusted fractions of hazardous compounds may be detected in the stack gas, and identified as PICs.

One of the facilities tested fired auxiliary fuel oil along with liquid and solid waste. A sample of the fuel oil was found to contain eight Appendix VIII compounds including five at concentrations exceeding 100 µg/g, as shown in Table 4. All of these compounds had been identified as POHCs in other waste feeds at this facility, but the auxiliary fuel was the primary contributor of two of the compounds. While this particular example does not influence the PIC emissions of the facility, had the same fuel oil been used at a facility where the compounds were not listed as POHCs in the waste feed, the undestroyed fraction would be detected in the stack as a PIC.

Compounds Occurring as Actual Combustion By-Products

The third mechanism to explain the presence of compounds identified as PICs is their formation as actual combustion by-products. Due to the extremely complex nature of waste feed and stack effluent, it is impossible to arrive at specific reactions or possible kinetics based simply on the results of this study. However, a review of the information collected is useful. The discussion which follows is presented in three parts, according to the category of combustion by-product.

Identifiable fragments of feed constituents which result from partial oxidation or simple substitution reactions.

An example in this category would be studies reporting the appearance of hexachlorobenzene as a by-product of PCB combustion.[2] Several of the plants MRI studied exhibited PICs which were unique to the type of waste being burned and were identifiable products of reactions of waste constituents. Two facilities which burned large quantities of aniline both exhibited high concentrations of nitrophenols in the stack. Only one plant showed measurable concentrations of polychlorinated benzenes in the waste, and this plant exhibited di-, tri-, and hexachlorobenzene in the stack. Likewise, chlorophenols were detected in the waste at only the one plant where ortho-, tri-, and pentachlorophenol were detected in the stack. These cases suggest that the compounds identified as PICs were formed as a result of specific constituents in the waste feed.

Reaction products which are the result of complex recombination or substitution reactions.

This category typically includes compounds of high molecular weight. High molecular weight compounds identified as PICs which might have resulted from complex reactions included naphthalene, fluoranthene, and pyrene.

Simple fragments which cannot be readily traced to any single reactant, but rather seem to be universal by-products of the combustion of organic compounds.

This category, which includes many low molecular weight compounds, was the most broadly represented among the plants studied. Each plant exhibited one or

TABLE 3. APPENDIX VIII COMPOUNDS FROM AMBIENT AIR

Compound		Concentration in stack gas (ng/L)	Potential contribution to stack gas concentration (%)
Benzene	PIC	130	4
Chlorobenzene	PIC	3.9	11
Toluene	POHC	14	50
Chloroform	POHC	20	4
1,1,1-Trichloroethane	POHC	0.3	100
Tetrachloroethylene	POHC	4.2	17
Trichloroethylene	POHC	2.5	21
Carbon tetrachloride	POHC	8.4	5

TABLE 4. APPENDIX VIII COMPOUNDS FOUND IN AUXILIARY FUEL OIL SAMPLE

Compound	Concentration (μg/g)
Toluene	1,500
Methylene chloride	440
Tetrachloroethylene	380
1,1,1-Trichloroethane	220
Methylene bromide	210
Benzene	91
Chloroform	23
Trichloroethylene	20

more fragments which might have resulted from the combustion of organic compounds. These included chlorinated methanes (chloromethane, methylene chloride, chloroform, and carbon tetrachloride), and chlorinated ethanes and ethylenes (1,1,1,-trichloroethane, trichloroethylene and tetrachloroethylene). In addition, bromoform was detected in high concentrations at one facility which was burning brominated wastes. Other fragments which were found as PICs could have resulted from the combustion of aromatics, and included benzene, phenol, toluene, and chlorobenzene.

Relative Contribution of Different PIC Mechanisms

Figure 3 summarizes, for each of the three PIC formation mechanisms discussed, the relative potential contribution of each to the total mass output of PICs. Low concentration POHCs in the waste feed potentially accounted for 0 to 68% of the total mass of PICs detected at each facility. The higher percentages were for the plants with the lowest total mass of PIC emissions. The stripping of THMs from the scrubber waters potentially accounted for up to 14% of the total mass of PICs detected. The rest of the compounds were most likely actual products of combustion reactions. Figure 3 also includes a bar which represents the percentage of the PICs which occurred most frequently and in the highest concentrations. The six compounds in this category accounted for a substantial percentage of the total mass of PIC output at most of the facilities tested. Table 5 lists these compounds, the concentration range measured, and how often they were detected.

CONCLUSIONS

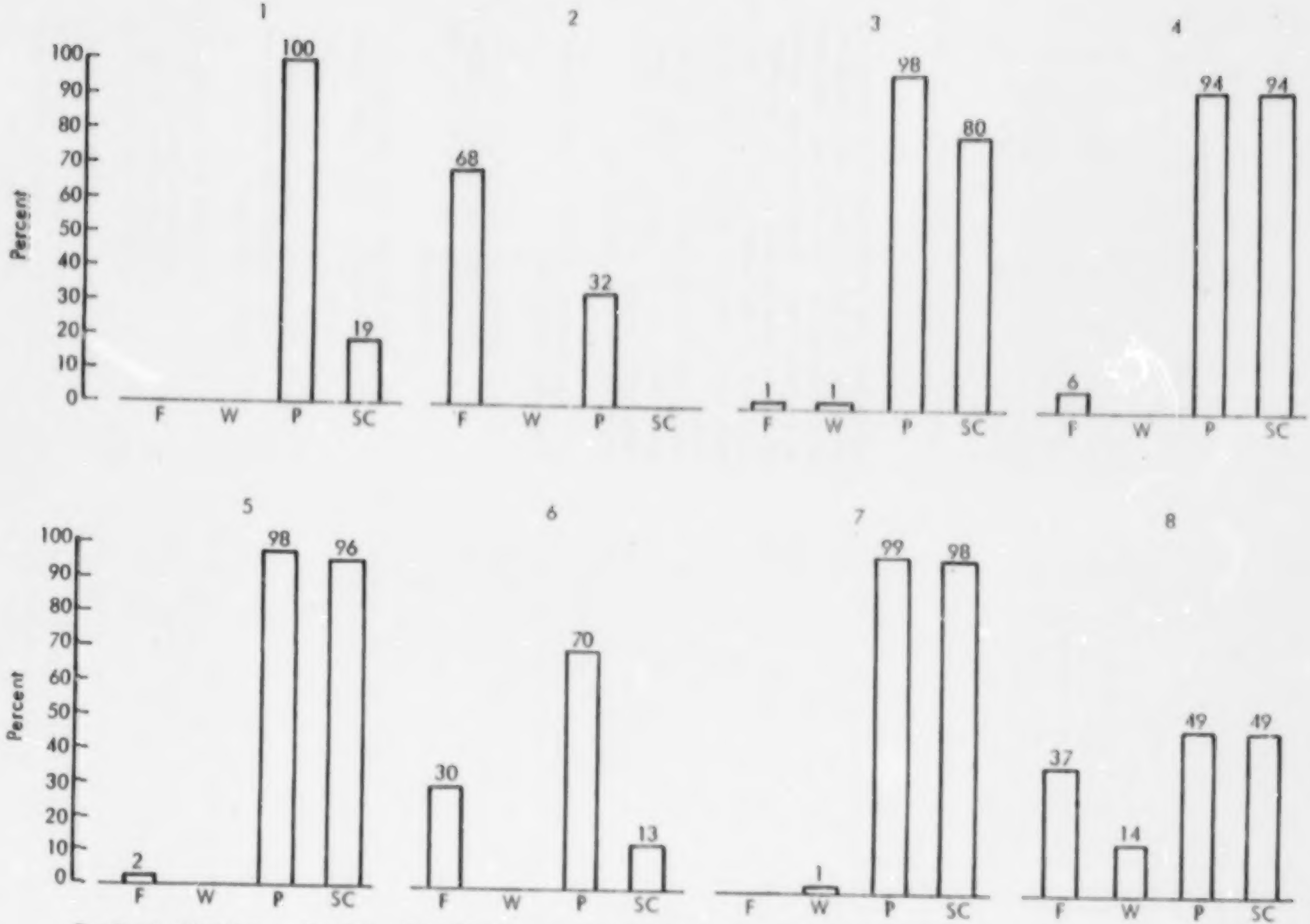
This program did not initially focus on identification of PIC mechanisms; thus, definite limits were imposed on interpretation of the PIC data. The discussion regarding appearance of PICs in the stack is fairly well documented for the case of the compounds stripped from the scrubber water, but otherwise the discussion of PIC formation mechanisms is somewhat conjectural. Possible mechanisms for formation of reaction byproducts, in particular, would require more information before being confirmed as explanations. More thorough investigation is also needed for the non-POHC fraction of the waste feed which, for the most part, remained unidentified in this study. Since the non-POHC fraction typically constitutes 30 to 90% of the waste feed, by-products from non-POHC combustion might prove very important in explaining the PIC phenomenom.

TABLE 5. SIX MOST COMMON PICs

Compound	Concentration range (μg/L)	No. of plants as a PIC
Chloroform	1.5 - 1,330	5
Benzene	13 - 670	6
Naphthalene	4 - 120	3
o-Nitrophenol	25 - 35	2
Bromoform	0.21 - 23	3
Phenol	5 - 19	2

In summary, general observations from the study are:

- Stack gas concentrations of PICs were typically as high as or higher than those for POHC compounds.
- PIC output rate infrequently exceeded 0.01% of POHC input rate.
- The three likely mechanisms that explain the presence of most PICs are:
  - Low DREs for Appendix VIII compounds present at low concentrations (< 100 μg/g) in the waste feed;
  - Input of Appendix VIII compounds to the system from sources other than waste feed; and



F = Feed, W = Waters, P = PICs, SC = Six Compounds; Numbers 1-8 identify the plants

Figure 3. Relative Contribution of Different PIC Mechanisms

- Actual products of incomplete combustion or products of complex side reactions.

- Benzene is the most likely compound to appear as a PIC, based on both frequency of occurrence and presence at higher concentrations.

- Measurement of Appendix VIII compounds at low concentrations in the waste feed, auxiliary fuel, and inflow streams to control systems is often necessary to explain the presence of PICs.

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PRELIMINARY ASSESSMENT OF COSTS AND CREDITS FOR HAZARDOUS WASTE CO-FIRING IN INDUSTRIAL BOILERS

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ABSTRACT

This paper outlines the results of an IRB-sponsored study to develop preliminary cost vs. credit information for hazardous waste co-firing in industrial boilers. An overview of the cost/credit estimating methodology is presented, along with pertinent background information on hazardous waste co-firing practices. Details of all cost estimates are provided in the project report, Reference 1.

BACKGROUND

The practice of burning hazardous wastes in industrial boilers has become increasingly popular over the past decade. The reasons for this trend are twofold:

(1) Increased prices for conventional fuels, favoring waste substitution or co-firing as a means of reducing fuel expenditures; and

(2) Stricter environmental regulations and higher costs for hazardous waste disposal by conventional methods, promoting waste co-firing as a means to eliminate or reduce waste disposal costs.

Two regulatory actions under the Resource Conservation and Recovery Act (RCRA) in particular have favored boiler co-firing as a hazardous waste disposal alternative. The first such action was the virtual ban on liquid waste landfilling which promoted thermal destruction (in incinerators, boilers, cement kilns, etc.) as the favored disposal method for hazardous organic liquids. The second regulatory action favoring boiler co-firing was the promulgation of emissions limitations for incinerators burning hazardous wastes. Since 1980, hazardous waste incinerators have been subject to Destruction and Removal Efficiency (DRE) requirements for hazardous organic constituents of the waste, particulate emission limitations, and HCl removal requirements. No such regulations have been imposed on boilers burning hazardous wastes.

This regulatory dichotomy has come under increasing attack over the last four years. From the standpoint of environmental safety and health, there is no conceptual difference between hazardous waste combustion in incinerators and boilers (although actual emission characteristics may vary). Boilers were originally exempted from regulation because the implied objective of waste co-firing was energy recovery, rather than waste disposal. However, this distinction has been clouded by the recent trend toward waste heat recovery in incineration facilities.

In order to assess the need for and impacts of regulations governing hazardous waste co-firing in boilers, EPA is currently conducting a Regulatory Impact Analysis (RIA) study. One of the major elements of this program is an economic assessment of the impacts of boiler performance standards and associated air pollution control requirements. The study addressed herein is intended to provide preliminary cost/ credit information for current boiler co-firing practices. As such, it serves as a precursor to the economic impact assessment phase of the RIA.

OBJECTIVES AND SCOPE

The underlying objective of the study is to provide a preliminary evaluation of the costs and credits associated with hazardous waste co-firing in industrial boilers. Specific objectives are as follows:

(1) Identify the major waste/boiler co-firing scenarios that need to be addressed for the purposes of the RIA.

(2) Identify the major costs and credits associated with boiler conversion to waste co-firing.

(3) Develop preliminary cost data for the major and most probable boiler retrofit activities.

(4) Develop a parametric approach to estimating retrofit costs, incremental operation and maintenance (O&M) costs, and credits so that cost/credit tradeoffs can be projected as a function of waste type, waste:fuel co-firing ratio, boiler design and capacity, and potential air pollution control requirements.

Due to the preliminary nature of the study, none of the objectives are addressed in a completely thorough or rigorous manner. The goal is simply to provide a basis for initial decision-making and more detailed future study.

CO-FIRING SCENARIOS EVALUATED

The range of hazardous waste co-firing scenarios addressed in the study is necessarily limited in terms of waste type, boiler design characteristics, capacity, and waste:fuel co-firing ratios. The evaluation is limited to those scenarios which best represent current practice and probable future practice.

Waste Characteristics

As a starting point, the evaluation is limited to hazardous organic liquid waste co-firing. This limitation is imposed because organic liquids are the prime candidates for boiler co-firing in terms of volume, handling characteristics, primary fuel firing compatibility, and compatibility with standard industrial boiler designs.

Second, the economic evaluation is based on in-house generation of the organic liquid wastes being co-fired. The assumption here is that industrial boiler operators do not routinely accept wastes from outside sources, thus functioning as commercial waste disposers.

The third major assumption is that the majority of wastes co-fired in industrial boilers possess desirable fuel properties. Heating values are assumed to be greater than or equal to 8,000-10,000 Btu/lb, such that the waste will support combustion. Water, ash, and halogen contents are also assumed to be reasonably low, so as to preclude flame quenching, excessive ash buildup on the boiler tubes, excessive bottom ash handling problems, and/or cold-end corrosion problems.

Finally, reasonable mid-range waste: primary fuel co-firing ratios are considered. The range is 10-50% waste with primary fuel, with the percentage based on gross heat input.

Boiler Designs and Capacities

The basic boiler designs considered in the study are those characteristic of the industrial size range (up to 250,000 lb/hr steam) originally designed to burn natural gas, distillate oil, residual oil, or a combination of these fuels. The three most common design types, addressed in the study, are as follows:

1. Scotch firetube, N-pass design, packaged boilers for natural gas, distillate oil, or combination gas/distillate oil firing. Single burner design, with no economizer or air heater. Typical capacities are 10,000 to 30,000 lb/hr steam, up to 50,000 lb/hr steam. Saturated steam up to 150 psig.

2. Watertube design for natural gas, distillate oil, gas/distillate, or gas/distillate/residual oil firing (with oil preheat equipment). Single or multiple burner design. Steam capacities of 20,000 to 100,000 lb/hr saturated at 125 to 250 psig design rating. Economizers not atypical at more than 50,000 lb/hr steam, but air heaters rare.

3. Watertube design with multiple burners for gas/oil firing. Steam capacities of 100,000 to 250,000 lb/hr and up, with turbogenerator steam pressures and superheat in the larger size ranges. Economizers typical, and possibly air heaters.

These boiler designs are most common (and compatible) for liquid waste co-firing, although a limited number of coal-fired boilers are also being used to co-fire hazardous liquids. Both stoker and pulverized coal-fired boiler conversion for waste co-firing are addressed to a minor extent.

CAPITAL REQUIREMENTS FOR BOILER SYSTEM RETROFIT

As indicated in the preceding section, one of the baseline assumptions of this study is that boilers co-firing hazardous wastes were originally designed to burn one or more conventional fossil fuels -- natural gas, oil, or coal. Therefore, an initial capital investment is required to retrofit a boiler for waste co-firing. This capital investment can be divided into three components:

(1) Addition of waste storage and feeding equipment,

(2) Boiler modification to accommodate the waste fuel, and

(3) Air pollution control device (APCD) addition for particulate/HCl removal, if required by regulation.

The total investment for retrofit is usually modest, unless air pollution control device addition is mandated. Costs are summarized below; details may be found in Reference 1.

Waste Handling and Feeding Equipment

Liquid wastes are usually transported from the process area to the boiler location by tank truck and pumped into a settling tank, or holding tank. Typical installed costs for individual 5,000, 10,000, and 20,000 gal tanks designed for hazardous liquid waste storage are approximately $34,000, $46,000 and $61,000 (December 1982), respectively.

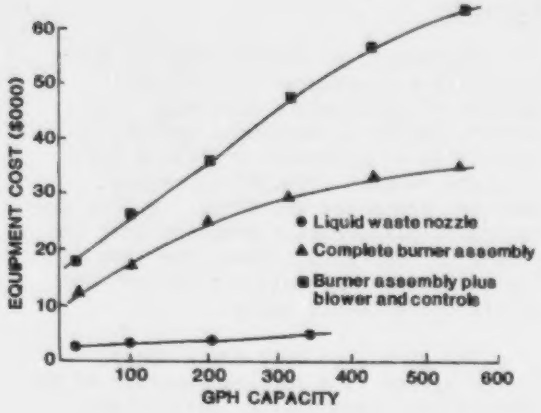
From the storage tank, wastes are usually pumped directly to the boiler through self-cleaning filters or dual strainers to remove any suspended solids. Dual feed pumps, costing $1,000 to $1,500 each, are desirable to provide redundancy in the event of equipment failure. Piping will cost $2,000 to $5,000. Costs for in-line filters can range from several hundred to several thousand dollars, depending on the flowrate, pressure, solids loading, and solids size distribution.

Boiler Retrofit

In any co-firing situations, retrofit at the boiler is a relatively minor consideration. High costs for boiler retrofit are usually incurred only when a completely new burner assembly, or burner assembly plus blower, damper, and control system is required. This may be the case when stoker or pulverized coal-boilers are retrofitted to burn liquid waste, or even when gas-oil fired boilers are converted over for waste co-firing.

Equipment cost vs. capacity data for three potential retrofit requirements are presented in Figure 1. The lower curve applies to one of the simplest retrofit cases: liquid waste nozzle addition/replacement. The costs shown in Figure 1 are the nozzles only; total installed costs including pressure and flow control valves, plus labor, can easily run two to three times the costs for the nozzles alone.

Figure 1. Burner Component and System Costs



The middle curve is for complete liquid fuel burner assemblies with natural gas firing capability built-in. The costs include pilot, spark ignition assembly, and damper assembly. The upper curve is for complete burner systems, including forced-draft blowers and master controls for flame safeguard, fuel modulation, air pressure and flow regulation.

Installation costs for burners and complete burner systems are typically 50% of the equipment cost. If structural modifications are required to install the burner, this installation cost can easily double.

Air Pollution Control Device Addition

Industrial boilers designed for natural gas or fuel oil firing are generally not equipped with any APCD's, including boilers co-firing hazardous liquid wastes. If Federal standards similar to the RCRA performance standards for incinerators were to be promulgated for boilers co-firing hazardous waste, it is likely that at least some boiler facilities would need to provide one or more APCD's for particulate and/or HCl removal. Obviously, this would depend on the ash content of the waste, chlorine content of the waste, and the regulatory requirements imposed.

It is impossible to predict industry trends relative to APCD addition at this point, should performance standards for particulate and/or HCl be promulgated. However, six scenarios can be envisioned:

(1) The waste being co-fired at the site in question contains negligible ash and chlorine, so APCD addition is unnecessary to comply with regulatory requirements.

(2) Chlorinated wastes are not being burned at the site, but particulate emissions exceed the standard as a result of waste co-firing. The mandated particulate removal efficiency is in the 95 to 99% range. In this case, a "cold-side," dry electrostatic precipitator (ESP) is the likely choice for particulate control.

(3) This scenario is identical to the previous one, except that the mandated particulate removal efficiency is more than 99.5%. In this case, a baghouse would probably be more economical than an ESP for particulate control due to the excessive plate area required for an ESP to achieve this efficiency. This is a generalization, however, which could be reversed by site-specific factors.

(4) The co-fired wastes do not contain significant ash, but chlorine is present in quantities such that the waste/fuel mix contains more than 0.5% organically-bound chlorine. In this case, a packed bed absorption system may be required for HCl removal. This is not considered a typical waste co-firing scenario, due to the adverse boiler corrosion impacts associated with burning chlorinated materials.

(5) The co-fired wastes contain significant ash and chlorine, such that particulate and HCl emission standards would both be violated. In this case, a venturi scrubber/packed bed absorption system would be the likely choice for air pollution control. Again, this is not considered a typical waste co-firing scenario for the reason stated above.

(6) Either particulate or HCl emission standards are exceeded, but the

boiler facility owner/operator chooses to eliminate waste co-firing rather than install the necessary air pollution control equipment.

These scenarios apply specifically to natural gas/fuel oil-fired boilers, but also to coal stoker-fired boilers in principle because stokers are usually equipped with no more than cyclonic separators for particulate control.

Electrostatic Precipitators

Electrostatic precipitators are one of the most common particulate control devices for large-scale utility boilers, and are well suited for industrial boiler retrofit to control particulate emissions unless (a) the gas is particularly wet, or (b) the gas contains significant HCl such that corrosion is a major potential problem. ESP advantages are high particulate collection efficiency at neglibile pressure drop.

Basic ESP costs are determined by two primary factors: insulation requirements and collection plate area requirements. Insulation requirements are a function of the cold-end temperature and gas dew point, i.e., condensation is undesirable due to the associated corrosion problem. For standard, uninsulated ESP's, cost is related to plate area by

$$P = 129{,}400 + 4.42A \qquad (1)$$

where P = purchased cost in June 1983 dollars
A = collection plate area, ft^2

If insulation is required,

$$P = 201{,}000 + 6.62A \qquad (2)$$

The basic equation for plate area is

$$A = Q \ln (1 - n)/w \qquad (3)$$

where Q = gas flow rate, cfs
n = fractional collection efficiency
w = drift velocity ft/s

For the purpose of this study, a drift velocity range of 0.1-0.3 ft/s is assumed.

The total installed cost for a basic ESP system is roughly double the purchased equipment cost.

Baghouses

Baghouses, or fabric filters, are also viable candidates for retrofit control of particulate emissions from boilers co-firing hazardous wastes, especially if extremely efficient particulate removal ($>99.5\%$) is needed. However, baghouses are subject to the same condensation/corrosion problems that can plague ESP operation; thus, the same limitations on gas moisture content and acidic constituents apply.

The purchased cost for a fabric filter system is a complex function of gas temperature, composition, particulate loading and size distribution, and system design features. Some of the major factors impacting costs are as follows:

(1) Type of system used:

- intermittent pressure, mechanical shaker cleaning
- continuous pressure, pulse jet cleaning
- continuous pressure, mechanical shaker cleaning
- continuous pressure, reverse air cleaning

(2) Type of bags (filter medium) used. The nominal operating temperatures of various fabrics are:

Cotton	180°F
Nylon	200°F
Acrylic, polyester	275°F
Nomex	425°F
Teflon	400°F
Fiberglass	550°F

(3) The need for insulation to prevent condensation

(4) The cloth area required (function of capacity and air-to-cloth ratio)

(5) Whether the system is custom built or standard.

The approach used to estimate a purchased equipment cost for a baghouse system, incorporating the design considerations listed above, does not lend itself to the simplification needed for this paper. Therefore, the reader should refer to Reference 1 for a procedure to estimate purchased costs for fabric filter systems. Installation costs may then be estimated as 95-100% of the purchased equipment cost.

Venturi Scrubber/Acid Gas Absorber Systems

If the gas is extremely wet or contains significant HCl as a result of co-firing chlorinated wastes, a venturi scrubber/acid gas absorber system would be the probable choice for particulate and/or HCl removal. Such a system would likely include a small nickel alloy quench to reduce the temperature of the boiler exit gas to saturation, a high nickel alloy venturi scrubber, a cyclonic separator and integral packed tower absorber of fiberglass construction, polypropylene tower packing, a caustic recycle system, a corrosion-resistant fan, and an acid-resistant stack. This type of system would be preferred in cases where wastes containing significant quantities of ash and/or chlorine are to be co-fired.

Total equipment cost, C, for this generic system is approximately given by the relationship derived in Reference 2:

$$\log C = 0.81 \log Q + 1.7$$

where Q is the inlet gas flowrate, ranging from 1,000 to 50,000 acfm. These costs are based on the assumption of a 30-in WC venturi pressure drop, which would be typical for hazardous liquid waste co-firing. If no venturi scrubber is needed, (i.e., little or no particulate control problem), the total equipment cost for the system is reduced by approximately 15%. Installation costs for this type of scrubbing system are typically about 50% of the equipment cost.

Indirect Costs

Indirect engineering and construction costs will be associated with any major retrofit activity such as burner system replacement/addition or APCD addition. These indirect costs are usually estimated as percentages of the total direct cost for equipment purchase and installation, as shown in Table 1.

TABLE 1. INDIRECT COST MULTIPLIERS

Indirect Cost	Percentage of Direct Cost
Engineering and supervision	10 to 20[a]
Construction and field expenses	10 to 20[b]
Construction Fee	7.5 to 10
Startup	1 to 3
Contingency	10
TOTAL	38.5 to 63

[a] 20% applies to ESP addition
[b] 20% applies to ESP or baghouse addition

These percentages are somewhat higher than would be expected for new facility construction because they apply to retrofit situations.

INCREMENTAL O&M COSTS

Incremental O&M costs for boiler operation are likely whenever waste, rather than fuel, is burned. These incremental costs can include increased consumption of electric power and water, operating labor, higher costs for residue disposal and maintenance, add-on costs for scrubbing chemicals, liquid nitrogen, and waste analysis, capital recovery charges, and taxes and insurance. Residue disposal and maintenance may be particularly significant and are discussed below.* The other O&M costs are discussed in Reference 1.

Ash Disposal

Co-firing hazardous waste with natural gas or fuel oil will in all likelihood increase the quantities of ash deposited on the furnace floor and the hopper fallout. Addition of baghouses or ESP's will also increase the quantities of ash that must be disposed. However, the major potential cost impact of hazardous waste co-firing is in ash characteristics, rather than the quantities of ash generated.

Under current RCRA regulations for incinerators and other treatment processes, any residue (e.g., ash) from the processing of a hazardous waste is, by definition, a hazardous waste as well. If this criterion was expanded to include ash from boilers co-firing hazardous waste, the cost impact could be significant (depending, of course, on the quantity of ash handled).

Conventional landfilling costs in major industrial areas throughout the U.S. range from about 0.1 to 1.0¢/lb for dry solid waste. Secure landfilling costs in the same areas range from 1.2 to 4.8¢/lb for the same type of waste. Typically, the secure landfilling costs are an order of magnitude higher. Total annual cost for ash disposal can be estimated using the general relationship:

Annual cost, $ =

(Ash content of waste, lb/lb)x

(Annual waste throughput, lb)x

(Landfilling cost, $/lb) (4)

Maintenance

Maintenance is potentially the most significant annual cost associated with co-firing hazardous wastes in boilers and also the most difficult to predict. Within the boiler itself, severe convective pass fouling and acid-gas corrosion are the two major concerns. The major conclusion pertinent to this study is that incremental boiler maintenance due to waste co-firing can range from virtually nil to the other extreme of catastrophic tube bundle failure. This type of corrosion-related problem is most likely when chlorinated, other halogenated, or phosphorous-bearing materials are burned and economizers or air heaters are incorporated in the boiler design. Likewise, fouling problems are most likely to occur when high ash content and/or alkali metal contaminated waste are burned in boilers with narrow, staggered tube spacings in the convective passes.

A considerably larger data base is available on APCD maintenance costs. Assuming that the proper type of equipment is specified for a given application, and that suitable materials of construction are used, the annual maintenance cost for ESP's and wet scrubbing systems is typically 5% of the equipment cost. A 5% multiplier can also be used to project hardware maintenance for baghouse systems, but the cost for bag replacement must also be considered.

CREDITS

The credits associated with co-firing hazardous wastes include the obvious fuel savings, plus elimination of certain on-site and/or contractor costs for dispoal of the waste.

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*This assumes that there are no air pollution controls added. If controls are added, then capital recovery costs are likely to be significant, and if the control is a scrubber, then the cost of caustics is important to consider.

Fuel Savings

Unless the full capacity of the boiler is not needed to satisfy plant steam requirements, one of the basic goals of waste co-firing is to maintain the same stream flow and quality. Therefore, the net fuel savings as a result of waste co-firing can be estimated by

$$Q_f = Q_w - Q_s \ (1/n_2 - 1/n_1) \qquad (5)$$

where Q_f = Net fuel savings, Btu/hr

Q_w = Heat input with waste, Btu/hr

Q_s = Desired (constant) heat output with steam, Btu/hr

n_1 = Boiler efficiency during baseline operation as measured by the ASME heat loss method

n_2 = Efficiency during co-firing

From equation (5) it is obvious that the fractional heat input with the waste must be greater than the efficiency loss associated with co-firing in order to realize a net fuel savings. Assuming that this is the case, net fuel savings is given by:

$$F_f = Q_f/HV_f \qquad (6)$$

where F_f = mass or volumetric fuel conservation rate

HV_f = fuel heating value

Based on these estimates, the boiler facility operating schedule, and local fuel prices, the annual fuel conservation credit can be calculated directly.

Waste Disposal Elimination

The savings associated with elimination of the waste disposal problem are highly variable, and not always easy to estimate. Because the vast majority of waste candidates for boiler co-firing are combustible liquids, it is likely that the alternative form of waste disposal would be incineration, either on-site or at a commercial waste disposal facility.

If the waste was burned in an on-site incinerator prior to boiler co-firing, the variable incineration costs such as auxiliary fuel, power, water, chemicals, residue disposal, labor, and maintenance would be eliminated by conversion to boiler co-firing. Fixed costs for the incineration facility would not be eliminated, however. Thus, the analysis must be done on a case-specific basis.

If the waste was shipped to an off-site incineration facility prior to boiler co-firing, the cost analysis is more straightforward. However, estimating an across-the-board cost savings is still difficult. Commercial waste disposal firms typically charge whatever the local market will bear, rather than a fixed percentage above cost. Moreover, most firms charge a premium for chlorine and ash content, and may offer a discount for volume and/or fuel value. Typical costs are 4¢ to 5¢/lb, although special wastes such as PCB oils may demand a price of 30¢/lb or even higher.

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HAZARDOUS WASTE PRETREATMENT AS AN AIR POLLUTION CONTROL TECHNIQUE

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ABSTRACT

There are many identified hazardous waste streams that contain volatile compounds that can be emitted to the atmosphere from landfills, surface impoundments, storage tanks, or other disposal facilities. One way to minimize or eliminate these emissions is to pretreat hazardous waste streams to remove volatile compounds.

This project examines specific hazardous and potentially hazardous waste streams (e.g., phenolic sludge from plastics production) and the technical applicability and economic feasibility of specific pretreatment techniques (e.g., steam stripping) for removing volatile compounds from them. In the absence of competitive removal mechanisms (such as biological decay), all the volatile constituents will ultimately be released to the atmosphere. The results show that air stripping, steam stripping, or evaporation (coupled with carbon adsorption of the offgases); steam stripping; and batch distillation are the most widely applicable pretreatment techniques. An example of air stripping coupled with carbon adsorption for removal of volatile constituents from hazardous waste streams containing aromatic solvents is given. The cost-effectiveness of pretreatment varies widely with waste stream characteristics and type of pretreatment, with typical values being between $0.099 and $2.00 per kilogram (kg) of volatile material removed. This paper is a summary of a more comprehensive report prepared by the Research Triangle Institute, which is unpublished as of May 1984. The reader is referred to the final report for Task 12-5 of EPA Contract 68-02-3149 for further information.

INTRODUCTION

The purpose of this study is to conduct a preliminary assessment of the technical and economic feasibility of various pretreatment techniques for the removal of volatile constituents from hazardous waste streams. This study was conducted in response to increasing concern over the potential adverse health and environmental consequences associated with emissions of volatile substances. Such emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs) are of particular interest. According to preliminary unpublished results from an Environmental Protection Agency (EPA) national survey of TSDFs conducted in 1981 (U.S. EPA 1983a), there are about 4,820 TSDFs in this country managing a total of about 151 billion liters, or approximately 100 million megagrams (Mg), of hazardous waste annually. Although no comprehensive estimate of the total volatile emissions from all domestic TSDFs has been reported, Breton et al. (1983) have estimated that nationwide emissions of 54 selected volatile compounds regulated under the Resource Conservation and Recovery Act (RCRA) may be as high as 1.6 million Mg per year. These emissions from TSDFs may represent as much as 19.5 percent of the total nationwide emissions of volatile organic compounds. These results, although based on limited data, suggest that emissions of volatile compounds from TSDFs are probably significant.

There are a number of sources within TSDFs from which volatile emissions can be emitted. These sources include

- Aerated impoundments
- Landfills
- Surface impoundments
- Cooling towers
- Storage tanks
- Waste handling and transfer operations.

Reasonably detailed data on stream composition and physical properties are required to evaluate pretreatment technology for removing volatile constituents. Available compilations of hazardous and potentially hazardous waste stream composition and generation rate information were evaluated to find the one most suitable for this study. The Waste Environmental Treatment (WET) Model (U.S. EPA 1983b) was judged to have the most pertinent information for an engineering assessment of this type. It is also the most comprehensive and, in spite of some limitations (e.g., volatile constituents are not identified for some streams and waste streams can vary in composition), the WET Model data were useful for assessing potential pretreatment techniques.

A thorough screening of current technology was conducted to determine which pretreatment techniques could be used for volatile constituent removal/ recovery. Nine broad engineering techniques were selected:

- Steam stripping
- Chemical oxidation
- Adsorption (liquid or gas phase)
- Biological treatment
- Ozonation/radiolysis
- Distillation
- Wet oxidation
- Solvent extraction
- Physical separation.

Techniques that are used primarily for ultimate destruction, such as incineration and pyrolysis, were excluded. The individual compatibility of these techniques and associated economics with all WET model waste streams was evaluated.

PRETREATMENT TECHNIQUES

For each pretreatment technique, there is a set of hazardous waste stream characteristics (or criteria) that determine if the technique is applicable to that stream. For example, one criterion for using liquid phase carbon adsorption pretreatment to remove volatiles is that the waste stream in contact with the adsorbent must not contain excessive concentrations of metallic ions or solids. Using this and other criteria, an appropriate WET Model stream has been selected, and a detailed example has been prepared to show how carbon adsorption pretreatment might be used. A similar analysis and an example have been prepared for each pretreatment technique listed above and are presented in the final report for this work, which will be available in the near future.

A distinction can be made between pretreatment processes that are applicable at the site of generation and processes that could be used at a TSDF that accepts waste materials from a variety of sources. At a typical TSDF, the waste streams are generally not segregated by source. Thus, pretreatment using carbon adsorption, steam stripping, and batch distillation, which has the capability of handling a variety of waste types, is likely to be most applicable at TSDFs.

EXAMPLE CASE--CARBON ADSORPTION

The adsorption of organic compounds from both liquid and gaseous phases onto activated carbon is a mature process technology with widespread use as an integral unit operation in such industrial manufacturing processes as corn syrup and pharmaceuticals production and sugar refining, in industrial and municipal wastewater treatment, in drinking water purification, in the separation and recovery of organic compounds from vapor streams, and in pollution control of atmospheric emissions. Although activated carbon has been and continues to be the dominant adsorbent used, other adsorbents such as resin or polymeric materials and zeolite molecular sieves have found increasing use for a number of special applications in recent years.

Since the selection of a pretreatment process depends on the nature of the hazardous waste stream, a number of different process configurations incorporating adsorption methods may be devised to accommodate a broader spectrum of hazardous waste streams. For this discussion, adsorption processes may be broadly classified into two groups: liquid phase and gas phase adsorption processes. Liquid phase adsorption usually involves the addition of relatively inexpensive powdered activated carbon (PAC) directly to the waste stream. The volatile material is adsorbed and the waste is disposed of without removal of the PAC; or, if desired, the PAC can be removed and regenerated. Gas phase adsorption systems (for pretreatment of hazardous wastes) include processes where volatile constituents are separated from the hazardous waste stream into a gaseous stream for subsequent removal by adsorption. This allows adsorption to be used on slurries and sludges that cannot be treated easily by liquid phase adsorption. The phase separation processes and adsorption process that were considered in this study are air and steam stripping and evaporation. For these gas phase systems, granular activated carbon (GAC) is the predominant adsorbent.

Process Description

The liquid phase activated carbon adsorption process involves two basic steps as shown in Figure 1. In Step 1 (adsorption), the waste stream contacts the carbon, which selectively adsorbs the hazardous material(s) and allows the purified stream to pass through. Step 2 (disposition of contaminated or spent carbon) represents a number of process options. When the carbon reaches its maximum capacity or when the effluent is unacceptable for discharge, the carbon is removed from the adsorber for disposal, destruction, or regeneration as established by the option selected under Step 2. In some cases, the carbon can be regenerated in such a way that the adsorbate is recovered. This may be important in pretreatment of hazardous wastes since the recovered volatile material may have some economic value (e.g., as a solvent).

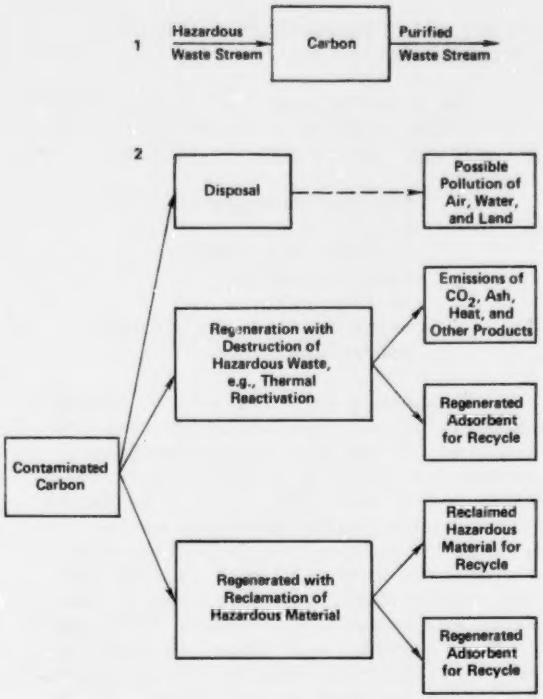
1
Hazardous Waste Stream
Carbon
Purified Waste Stream
2
Disposal
Possible Pollution of Air, Water, and Land
Regeneration with Destruction of Hazardous Waste, e.g., Thermal Reactivation
Emissions of CO_2, Ash, Heat, and Other Products
Regenerated Adsorbent for Recycle
Contaminated Carbon
Regenerated with Reclamation of Hazardous Material
Reclaimed Hazardous Material for Recycle
Regenerated Adsorbent for Recycle

Figure 1. Steps in carbon adsorption.

Process Operation

The technical suitability of a waste stream for carbon adsorption pretreatment depends mainly on its physical form and the type and relative concentration of constituents. However, other factors that affect the treatment economics often dictate which streams are actually feasible for carbon treatment; such factors include the required degree of solute removal, waste throughput rate, and carbon utilization. The discussion below is intended to provide guidance in prescreening waste streams for carbon treatment. Selection should be based on laboratory adsorption and regeneration studies with the actual waste stream.

In general, carbon adsorption is applicable only to single-phase fluid streams; specifically, liquid solutions and gas mixtures. Although both aqueous and nonaqueous streams may be treated with carbon, liquid phase waste treatment applications to date have been confined to aqueous streams.

The suspended solids level in the waste influent to the carbon contactors (adsorbers) generally should be less than 50 ppm for optimum process operation. Although suspended solids levels up to

2,000 ppm may be handled in special equipment, stream prefiltering is usually employed with these streams.

The amount and type of nonvolatile organics and dissolved inorganics must also be considered. Oil and grease in the waste stream should be less than 10 ppm to avoid carbon fouling. High levels of dissolved inorganics may cause such problems as scaling (corrosion) and serious loss of carbon activity with thermal carbon reactivation. In some cases, however, these problems may be mitigated through pH control and softening of the waste influent or by acid washing the carbon before reactivation.

Technically, a high concentration of solute(s) in the waste influent does not limit carbon adsorption treatment. However, in actual practice the most concentrated influent to be treated on a continuous basis contained approximately 10,000 ppm total organic carbon (TOC). Nevertheless, higher solute concentrations up to 15 percent may possibly be carbon treated. This limit of 15 percent solute concentration is strictly a practical and economic one. Technically, there is no real limit to solute concentrations that are treatable by carbon adsorption. In addition, when the carbon is regenerated, the higher solute influent concentrations result in higher loading of the carbon (mass solute adsorbed/mass of carbon) and thus less frequent regeneration may be required.

The flow rate of the waste stream does not affect the technical aspects of carbon treatment, but it does have a major impact on treatment economics. Carbon treatment benefits significantly from economies of scale, especially where thermal reactivation is used. If carbon usage is less than 500 kg/day, then the economics generally favor disposal of the spent carbon. At carbon usage over 4,000 kg/day, onsite thermal reactivation is usually feasible. Where carbon rates are between 500 and 4,000 kg/day, offsite reactivation should be considered.

The identification of waste streams that are suitable for carbon treatment is more difficult when multicomponent solutes are present. Some "secondary" constituent may interfere with the adsorption of the solute(s) of interest. For example, long-chain organic soaps were found to cause poor carbon adsorption performance on a wastewater stream from a polyvinyl chloride production plant (U.S. EPA 1971). Thus, preliminary laboratory studies on the actual waste stream are essential in prescreening candidate waste streams for carbon treatment.

In summary, the following characteristics may be used as guidelines to identify wastes streams that are likely candidates for carbon treament:

- Aqueous waste streams with organic solute concentrations that are less than 15 percent.
- Waste streams where the aggregate concentration of high molecular weight nonvolatile organics is substantially lower than the concentration of the volatile organics.
- Waste streams where suspended solids are less than 50 ppm if the stream is not prefiltered and less than 2.5 percent if prefiltering is used.
- Waste streams where oil and grease concentrations are less than 10 ppm.
- Waste streams where the concentration of dissolved inorganics is low (less than 100 ppm) unless waste stream preconditioning and spent carbon washing before reactivation operations are included.

The removal efficiency of carbon treatment can be controlled to practically any level through the design of the carbon contactor. Typical carbon treatment efficiencies are better than 99 percent with influent concentrations below 1,000 ppm. At higher influent concentrations, removal efficiencies can exceed 99.99 percent removal to yield effluent concentrations at several ppm. Of course, as with most alternative treatment processes, carbon treatment removal efficiencies must be compared to capital and operating costs, which increase dramatically as efficiencies approach 100 percent.

Process Economics

Several variables and/or alternatives in the design and operation of a carbon treatment system can have a major impact on the economics of the process. These factors include:

- Type of carbon (GAC or PAC)
- Flow rate
- Contact time
- Process configuration (series, parallel, or moving bed)
- Number of stages
- Flow direction (packed or expanded; upflow or downflow).

WET Model Example

Waste stream 02.02.14 from the WET Model was selected as an example to show a typical carbon adsorption system design, associated material balances, and treatment economics.

This stream, with a nominal rate of 426,000 kg/day (17,750 kg/h, based on 365 days per year operation) contains benzene, toluene, and phenol at concentrations ranging from 3,000 to 5,000 ppm. Although these concentrations are on the upper range of the concentrations currently being treated in commercial practice, GAC has been shown to be effective for these constituents at these levels. The composition of WET stream 02.02.14 is given in Table 1.

Table 1. Composition of WET Stream 02.02.14, Quench Blowdown from Ethylene Production by Thermal Cracking of Heavy Liquids

Component	Mass fraction	Flow rate, kg/h
Benzene	0.005	88.8
Phenol	0.003	53.3
Toluene	0.004	71.0
Solids	0.01	177.5
Water	0.98	17,359.5
Total	1.002	17,750.1

The process flowsheet for carbon adsorption pretreatment of the above waste stream is shown in Figure 2. The process design and configuration shown includes waste stream preconditioning, moving-bed adsorption, thermal reactivation, and furnace offgas cleaning units. The preconditioning system is designed to remove suspended solids to below 50 ppm and to allow pH adjustment of the waste influent for maximum adsorption efficiency of the carbon.

The material balance for the pretreatment example is shown in the tabular portion of Figure 2. Although the material balance indicates essentially 100 percent removal of the three organics, in actual practice the waste effluent (stream No. 8) may contain these constituents at concentrations of several ppm.

The major process uncertainties in the design of this carbon adsorption are: (1) the equilibrium capacity of the carbon for the three organics in a multicomponent aqueous solution of this particular composition, (2) the adsorber residence (retention) time, and (3) the carbon recirculation rate. For this case, a carbon loading of 0.3 kg adsorbate/kg carbon and a minimum adsorber residence time of 30 minutes was assumed. Also, to size the reactivation furnace, a furnace residence time of 30 minutes was assumed. These assumptions are consistent with the ranges used in current practice.

Economics

The capital and operating costs for the above example case were based on 24-h/day, 330-day/yr operation, an adsorber design capacity of 200,000 gal/day (126 percent of waste stream rate including recycle streams to the adsorber), and reactivation furnace throughput rate of 25,500 kg carbon/day. The capital costs of the major components of the carbon treatment system including support equipment, installation, engineering, legal, financing, and administrative costs are presented in Table 2.

The annual operating costs for the system are also included in Table 2. The major operating costs include: labor, electricity, fuel (natural gas), maintenance materials, and carbon makeup.

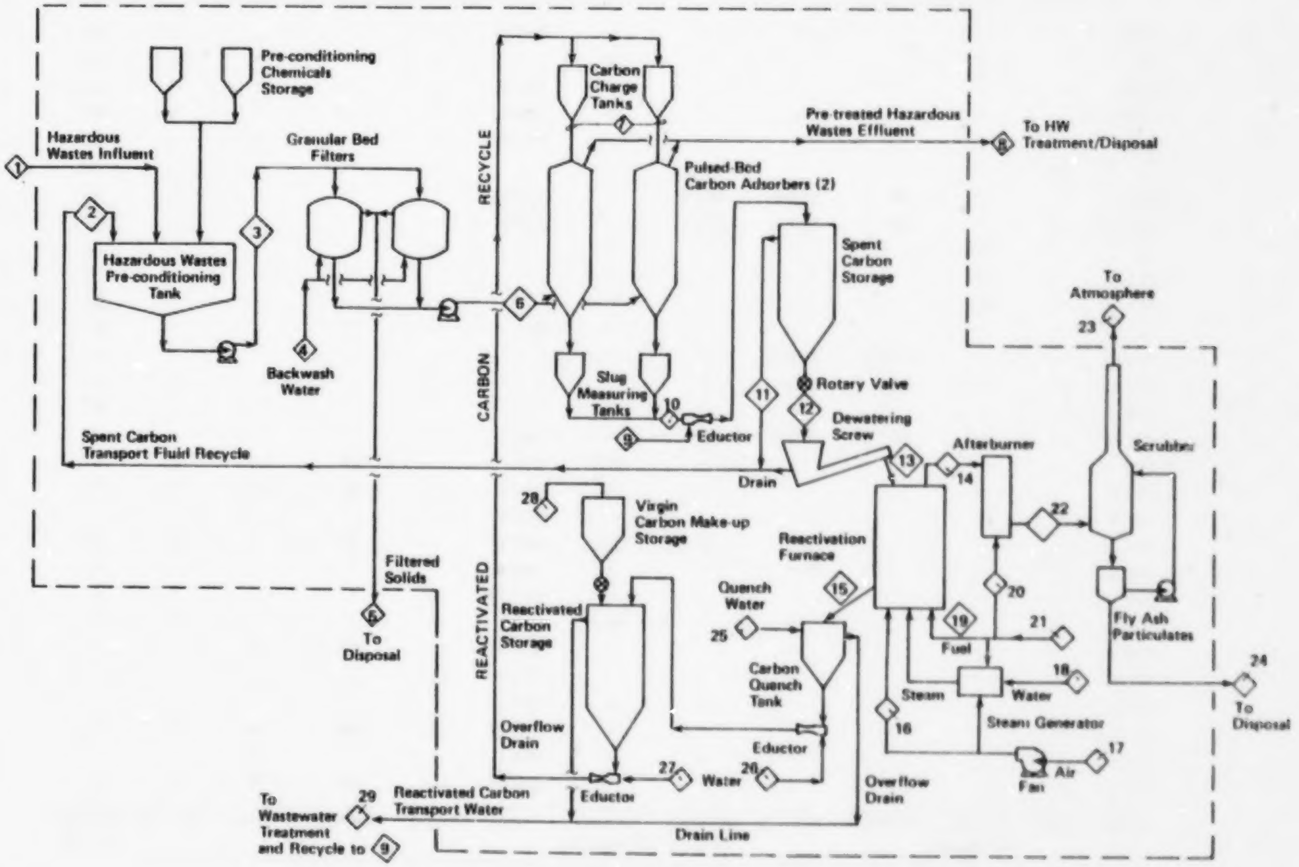
Pre-conditioning Chemicals Storage
Hazardous Wastes Influent
1
2
Hazardous Wastes Pre-conditioning Tank
3
Granular Bed Filters
4
Backwash Water
5
To Disposal
Filtered Solids
6
RECYCLE
CARBON
REACTIVATED
Carbon Charge Tanks
7
Pre-treated Hazardous Wastes Effluent
8
To HW Treatment/Disposal
Pulsed-Bed Carbon Adsorbers (2)
Slug Measuring Tanks
9
10
Eductor
11
Spent Carbon Storage
Rotary Valve
12
Dewatering Screw
Drain
Spent Carbon Transport Fluid Recycle
13
14
Afterburner
Reactivation Furnace
15
16
Steam
Steam Generator
17
Air
Fan
18
Water
19
Fuel
20
21
22
Scrubber
23
To Atmosphere
Fly Ash Particulates
24
To Disposal
25
Quench Water
Carbon Quench Tank
Eductor
26
Water
27
Water
Eductor
28
Virgin Carbon Make-up Storage
Reactivated Carbon Storage
Overflow Drain
Overflow Drain
Drain Line
Reactivated Carbon Transport Water
29
To Wastewater Treatment and Recycle to 9

Figure 2. Process flow sheet for carbon adsorption pretreatment to remove volatile constituents from hazardous waste.

Key to Figure 2

Stream Number	Stream Components (kg/h)											
	Toluene	Phenol	Benzene	Solids	Water	Activated Carbon	Carbon Dioxide	Nitrogen	Oxygen	Methane (fuel)	Ash	Total
1	71	53	89	178	17,360	–	–	–	–	–	–	17,750
2	–	–	–	–	7,385	–	–	–	–	–	–	7,385
3	71	53	89	178	24,745	–	–	–	–	–	–	25,136
4	–	–	–	–	1,557	–	–	–	–	–	–	1,557
5	–	–	–	177	1,557	–	–	–	–	–	–	1,734
6	71	53	89	1	24,745	–	–	–	–	–	–	24,959
7	–	–	–	–	1,657	710	–	–	–	–	–	2,367
8	–	–	–	<1	24,745	–	–	–	–	–	–	24,745
9	–	–	–	–	6,651	–	–	–	–	–	–	6,651
10	71	53	89	–	1,657	710	–	–	–	–	–	2,580
11	–	–	–	–	6,154	–	–	–	–	–	–	6,154
12	71	53	89	–	2,154	710	–	–	–	–	–	3,077
13	71	53	89	–	923	710	–	–	–	–	–	1,846
14	–	–	–	–	1,346	–	790	2,580	55	–	17	4,788
15	–	–	–	–	–	667	–	–	–	–	–	667
16	–	–	–	–	–	–	–	2,580	686	–	–	3,266
17	–	–	–	–	–	–	–	9,463	2,516	–	–	11,979
18	–	–	–	–	710	–	–	–	–	–	–	710
19	–	–	–	–	–	–	–	–	–	158	–	158
20	–	–	–	–	–	–	–	–	–	127	–	127
21	–	–	–	–	–	–	–	–	–	331	–	331
22	–	–	–	–	1,631	–	1,138	4,485	55	–	17	7,326
23	–	–	–	–	1,631	–	1,138	4,485	55	–	–	7,309
24	–	–	–	–	–	–	–	–	–	–	17	17
25	–	–	–	–	1,945	–	–	–	–	–	–	1,945
26	–	–	–	–	4,007	–	–	–	–	–	–	4,007
27	–	–	–	–	4,007	–	–	–	–	–	–	4,007
28	–	–	–	–	–	43	–	–	–	–	–	43
29	–	–	–	–	9,000	–	–	–	–	–	–	9,000

TABLE 2. CAPITAL AND OPERATING COSTS FOR CARBON ADSORPTION PRETREATMENT WITH THERMAL REACTIVATION OF THE CARBON FOR WET MODEL STREAM 02.02.14

Capital Costs	
Influent pump station	21,000
Carbon adsorption system (2 pulsed-bed contactors)	181,000
Carbon regeneration system (fluidized-bed furnace)	1,925,000
Carbon inventory (150,000 lb @ $0.85/lb)	128,000
Construction costs[a]	925,000
Total Installed Cost	$3,180,000
Annualized Operating Cost	
Operating labor (36,000 man-hours @ $15/m-h)	540,000
Maintenance (5% of capital cost)	159,000
Electricity (824,000 kWh @ $0.05/kWh)	41,200
Steam (13,680,000 lb @ $4/1,000 lb)	54,700
Fuel (1,430,000 therms @ $0.59/therm)	840,000
Water (20,800,000 gal @ $0.40/1,000 gal)	8,300
Carbon makeup (829,000 lb @ $0.85/lb)	704,700
Taxes, insurance, administration (4% of capital cost)	127,200
Capital recovery (16.3%; 10% over 10 years)	518,300
Total Operating Costs	$2,993,400
Product Recovery Credit	0
Net Operating Costs	$2,993,400
Waste treated (kg/yr)	155,490,000
Total volatiles removed (kg/yr)	1,865,880
Unit treatment cost ($/kg waste treated)	0.019 $/kg
($/kg volatiles removed)	1.60 $/kg

[a] Construction fee (10%), contingency (15%), engineering (15%), startup (1%).

Advantages and Disadvantages

The major advantages of carbon pretreatment are:

- It is a mature technology in commercial use for waste treatment applications.
- Carbon adsorption can handle a broad range of organic constituents and concentrations.

The disadvantages of carbon pretreatment include:

- Carbon adsorption treatment, especially with thermal reactivation, is a complex and labor-intensive operation.
- Carbon adsorption has substantial operating costs.

Table 3 shows the results of the analysis of other types of pretreatment processes. Applicable pretreatment processes are shown for some typical waste types that may contain volatile constituents. This table shows that air stripping, steam stripping, or evaporation (coupled with carbon adsorption of the offgases); steam stripping; and distillation are the most widely applicable techniques for volatile removal.

Insofar as the hazardous waste streams are typical of the application, the pretreatment technique, the volatile removal efficiency (kg volatile removed/kg volatile in the stream), unit cost

TABLE 3. APPROPRIATE PRETREATMENT PROCESS BY WASTE TYPE

Waste type	Applicable pretreatment process(es)
Organic liquids	Distillation
Aqueous, up to 20% organic	Steam stripping Solvent extraction
Aqueous, less than 2% organic	Steam stripping Steam stripping with carbon adsorption Resin adsorption Air stripping with carbon adsorption Ozonation/radiolysis Wet oxidation Biological treatment
Sludge with organics	Air stripping with carbon adsorption Evaporation with carbon adsorption Ozonation/radiolysis Wet oxidation Chemical oxidation Evaporation with carbon adsorption
Some sludge in organic or aqueous stream	Physical separation

($/kg stream treated), and cost-effectiveness ($/kg of volatile removed) are typical of what may be expected if the pretreatment technique were used on other streams of a similar nature.

One further important result of this study is an engineering judgment regarding the most applicable pretreatment technique(s) for all WET Model streams. This is presented (in the final report for this project) in a matrix that matches the 12 pretreatment techniques considered in this report with all WET Model streams that contain volatile constituents. Based on this matrix, the following pretreatment techniques are considered most applicable for removing volatile constituents from the WET Model waste streams.

- Air stripping, steam stripping, or evaporation/carbon adsorption
- Steam stripping
- Batch distillation.

SUMMARY AND CONCLUSIONS

In summary, this paper is a preliminary examination of various pretreatment techniques for the removal of volatile compounds from hazardous waste streams identified in one data base. Although the conclusions and analyses herein may not be regarded as final, this paper does provide insight into the potential applicability of pretreatment to reduce emissions of volatile compounds from TSDFs.

The conclusions of this investigation are:

- An analysis of potential air emissions from treatment, storage, and disposal of 72 hazardous waste streams indicated that a substantial fraction of volatile hazardous components could be emitted to the atmosphere from landfills, land treatment facilities, surface impoundments, and cooling towers. It is reasonable to assume that in many cases, removal of organics by pretreatment would cause a comparable reduction in air emissions.

- Pretreatment of these hazardous waste streams could remove most (90 to 99 percent) of the volatile materials. A number of alternative processes are available for pretreatment for most of the waste streams.

- The cost-effectiveness varied from $70 to over $2000/Mg of volatiles removed. The cost-effectiveness of pretreating specific waste streams is not necessarily in the same range as the example cases. The actual cost-effectiveness would depend on the chemical and physical characteristics of the waste stream(s), the design capacity of the pretreatment system, and the degree of volatile removal required.

- Pretreatment techniques using carbon adsorption, steam stripping, or batch distillation are the most applicable ones for the WET model streams evaluated. This judgment considers cost, the range of applicability, and the extent to which the technology has been demonstrated.

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PROGRAMS OF THE INDUSTRIAL WASTE COMBUSTION GROUP AT THE U.S. EPA CENTER HILL FACILITY

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ABSTRACT

The primary focus of EPA's inhouse Thermal Destruction research being conducted at their Center Hill Facility (part of their Cincinnati-based Industrial Environmental Research Laboratory) is to:

- Establish how combustion variables affect failure of a simulated hazardous waste incinerator or a simulated industrial boiler that co-fires hazardous waste with conventional fuel to achieve 99.99% DRE (Destruction and Removal Efficiency);
- Determine how, when and why PIC's (Products of Incomplete Combustion) are formed (e.g., too low an oxygen concentration or too low an operating temperature) and to determine how or whether they can be subsequently destroyed or removed (e.g., by secondary combustion or scrubbing/adsorption techniques); and
- Determine which organic chemicals are the hardest to burn [this will assist in making better selections of POHCs (Principal Organic Hazardous Constituents)].

Key research being done at Center Hill features:

- Conducting parametric testing, in bench-scale and mini-pilot combustors on simulated hazardous waste mixtures to determine the range of operating conditions under which efficient hazardous waste destruction can be expected and where PICs can be minimized. The combustion equipment located there consists of a bench-scale non-flame "TDU-GC" (Thermal Destruction Unit-Gas Chromatograph), a "Microspray Reactor" (a laminar-flow intermediate-size unit having a quiescent flame), a "Turbulent Flame Reactor" (a larger, mini-pilot, water-jacketed unit having the ability to induce turbulence into a flame), and a "Controlled Temperature Tower" (a refractory-lined, 4-foot outside diameter by 7-foot high reactor which provides for turbulence, secondary combustion and simulated cold walls). The operation of each of these units will be supported by an onsite GC/MS to provide comprehensive analytical capability.
- Examining key combustion variables to determine their impact on POHC DRE's and on PIC formation and destruction. Key variables will include residence time, operating

temperature, degree of turbulence, degree of atomization, pressure drop across the burner nozzle, oxygen concentration, air-to-fuel ratio, waste-to-fuel ratio, waste mixture constituent impacts, secondary combustion impacts, and the impacts resulting from quenched destruction reactions due to cold walls in combustors.

- Carrying-out parametric testing on key process variables attendant to the operation of a two-stage air pollution control system (consisting initially of a packed-bed scrubber for HCl control and an activated carbon bed for unburned hydrocarbon removal) to define the amounts of pollutant removal that is possible (i.e., to provide data on the "R" part of the DRE).

Specific hypotheses that will be addressed in this In-House Thermal Destruction Research Program include:

(1) The DRE performance of a hazardous waste combustor can be predicted by CO/CO_2 or THC (total hydrocarbon) in the exhaust gas; consequently, continuous monitoring based on one or more of these parameters may be suitable as a compliance monitoring technique.

(2) Flame cooling (due to flame proximity to cooler heat transfur surfaces) and post-flame heat heat loss can have a marked effect on overall DRE performance and on PIC formation.

(3) The standardized POHC test mixture used in EPA's ongoing full-scale test burns is a representative mixture for characterizing the DRE and PIC formation/destruction performance of a given combustor across a range of operating conditions.

(4) High levels of PIC's can be fed into the post-flame zone during the combustion of hazardous waste, and they can be significantly lessened there due to the large gas residence times that exist in that zone, or the opportunity for secondary combustion there.

(5) A two-stage scrubber/carbon bed system can effectively remove HCl and organics formed in or passed through thermal destruction devices burning hazardous wastes.

The first three hypotheses will be tested in the flame-mode Turbulent Flame Reactor/Controlled Temperature Tower, the fourth hypothesis in the non-flame TDU-GC system and the fifth, obviously, in the scrubber system discussed above.

DETERMINATION OF THE THERMAL DECOMPOSITION PROPERTIES OF 20 SELECTED HAZARDOUS ORGANIC COMPOUNDS

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ABSTRACT

Laboratory determined thermal decomposition profiles and kinetic data for a list of 20 selected hazardous organic compounds are reported. All data were obtained in flowing air at mean gas-phase, high-temperature zone residence times ranging from one to six seconds. The extrapolated temperatures required for 99.99% destruction of the parent compound at two seconds mean residence time, $T_{99.99}(2)$, ranged from 600°C for 1,1,1-trichloroethane to 950°C for acetonitrile. The processes and parameters potentially controlling incineration efficiency are discussed, and four previously proposed methods of ranking compound incinerability are reviewed.

The possible chemical mechanisms for destruction of hazardous organic compounds are examined and used to explain trends in the experimentally determined thermal decomposition data. It is proposed, through proper application of the principles of organic chemistry, kinetics, and physics, that laboratory, gas-phase thermal decomposition data generated under controlled conditions can be incorporated into models of full-scale incineration, serve as a viable ranking of waste incinerability, and used to predict the formation of products of incomplete combustion.

INTRODUCTION

The ultimate goal of hazardous waste incineration is to destroy the waste material with as high a destruction efficiency (DE) as possible. Under the Resource Conservation and Recovery Act (RCRA) of 1976, an incinerator operator must show that the facility can adequately destroy those hazardous waste constituents which are most difficult to incinerate. In theory, the permit writer will select compounds within the mixture which are of sufficient toxicity, concentration, and thermal stability so as to be designated as principal organic hazardous constituents (POHCs). It must then be shown, possibly by trial burn, that the designated POHCs can be destroyed or removed by the particular incineration system to a destruction and removal efficiency (DRE) of 99.99 percent.

The development of a ranking of the incinerability for compounds which are candidates for POHC selection is of obvious utility. The US-EPA currently is using a ranking based on the heat of combustion per gram of pure compounds. This method has received considerable criticism, and the development of an alternative ranking scheme is of a very high priority to the EPA.

Experimentally determined gas phase thermal stability under controlled laboratory conditions has been proposed as an alternative ranking method. This report presents the results of the laboratory determination of the gas phase thermal decomposition properties of twenty (20) hazardous organic compounds. The compounds were selected by the EPA based on their frequency of occurrence in hazardous waste streams, apparent prevalence in the stack effluent, and representativeness of the spectrum of hazardous organic waste materials.

EXPERIMENTAL PROCEDURES

All of the experimental data presented in this study were generated using the thermal decomposition unit-gas chromatographic (TDU-GC) system which was designed and built with funding provided by the US-EPA (Cooperative Agreement No. 807815-01-0) [1]. Samples of the 20 compounds were prepared and introduced to the system by several procedures depending upon their physical state and vapor pressure.

To initiate a test, the sample is introduced into the system and gradually vaporized in a flowing gas stream (i.e., nitrogen, air, or nitrogen/oxygen mixtures). The vaporized sample passes through a controlled, high-temperature tubular reactor where it undergoes thermal decomposition. The products evolving from the thermal decomposition of the compound and the remaining parent compound are swept into a Varian VISTA 4600 high-resolution gas chromatograph for analysis. The sample insertion chamber, the reactor, and the entire transport system are fabricated of fused quartz to minimize interaction with the sample.

In the TDU-GC system, the sample is deposited in a sample insertion chamber which is packed with quartz wool. The chamber is slowly heated to 250°C to 300°C by applying a linear temperature program (10-20°C/min). The sample molecules are thermally desorbed and gradually swept into the thermal reactor.

The sample emerging from the reactor is trapped at the head of the chromatographic column by maintaining the GC oven at a cryogenic temperature (~minus 30°C). A 15 meter dimethylsilicone chemically bonded stationary phase fused silica capillary column in conjunction with a flame ionization detector was used in the majority of the investigation.

For the ethane analyses, Tedlar bags were used to capture the reactor effluent at the splitter. The captured gas was subjected to analyses using a Varian Aerograph Series 1800 gas chromatograph equipped with one meter x 4.0 mm ID packed column (5 Å molecular sieve, 45/60 mesh) operated isothermally at 150°C. This system was utilized to ensure resolution of the three C_2 hydrocarbons.

RESULTS

For each of the twenty (20) test compounds, the fraction of the feed material undestroyed at a given set of temperatures and mean reactor residence times ($\bar{t}_r$) was determined. This resulted in the generation of what may be termed thermal decomposition profiles, i.e., a semilogarithmic plot of fraction remaining (f_r) vs. the reactor temperature (°C) at constant residence time. Thermal decomposition profiles were generated in flowing air at four mean residence times, $\bar{t}_r$ = 1.0, 2.0, 4.0, and 6.0 seconds. An example of the determination of this family of profiles is given in Figure 1 for chloroform. The thermal decomposition profile for chloroform is representative of the great majority of the compounds tested and serves to illustrate several features.

The data for the test compounds have been summarized in Table 1 with entries for the temperature for the onset of decomposition, T_{onset} (2) (°C), the interpolated temperature for 99% destruction, T_{99} (2) (°C), and the extrapolated temperature for 99.99% destruction, $T_{99.99}$ (2) (°C). All these values are for $\bar{t}_r$ = 2.0 seconds in flowing air. Using only the data presented in this table, the thermal decomposition profile for the compounds may be approximately reconstructed. The table lists the compounds in order of decreasing temperature required for 99% destruction efficiency. A slight reordering occurs if $T_{99.99}(2)$ is used for ranking. However, the numerical differences for the reordered compounds are small.

For the conditions possibly encountered during gas-phase thermal decomposition in an incinerator (600°C to 1,400°C and oxygen levels of 0.1 to 21%), two possible global decomposition pathways

TABLE 1. SUMMARY OF THERMAL DECOMPOSITION DATA

Compound	Empirical Formula	T_{onset}(2) (°C)	T_{99}(2) (°C)	$T_{99.99}$(2) (°C)	$A(s^{-1})$	E_a (kcal/mole)
Acetonitrile	C_2H_3N	760	900	~950	4.7×10^7	40
Tetrachloro-ethylene	C_2Cl_4	660	850	920	2.6×10^6	33
Acrylonitrile	C_3H_3N	650	830	860	1.3×10^6	31
Methane	CH_4	660	830	870	3.5×10^9	48
Hexachlorobenzene	C_6Cl_6	650	820	880	2.5×10^8	41
1,2,3,4-Tetrachlorobenzene	$C_6H_2Cl_4$	660	800	850	1.9×10^6	30
Pyridine	C_6H_5N	620	770	840	1.1×10^5	24
Dichloromethane	CH_2Cl_2	650	770	780	3.0×10^{13}	64
Carbon Tetra-chloride	CCl_4	600	750	820	2.8×10^5	26
Hexachlorobuta-diene	C_4Cl_6	620	750	780	6.3×10^{12}	59
1,2,4-Trichloro-benzene	$C_6H_3Cl_3$	640	750	790	2.2×10^8	39
1,2-Dichlorobenzene	$C_6H_4Cl_2$	630	740	780	3.0×10^8	39
Ethane	C_2H_6	500	735	785	1.3×10^5	24
Benzene	C_6H_6	630	730	760	2.8×10^8	38
Aniline	C_6H_7N	620	730	750	9.3×10^{15}	71
Monochlorobenzene	C_6H_5Cl	540	710	780	8.0×10^4	23
Nitrobenzene	$C_6H_5NO_2$	570	670	700	1.4×10^{15}	64
Hexachloroethane	C_2Cl_6	470	600	640	1.9×10^7	29
Chloroform	$CHCl_3$	410	590	620	2.9×10^{12}	49
1,1,1-Trichloro-ethane	$C_2H_3Cl_3$	390	570	600	1.9×10^8	32

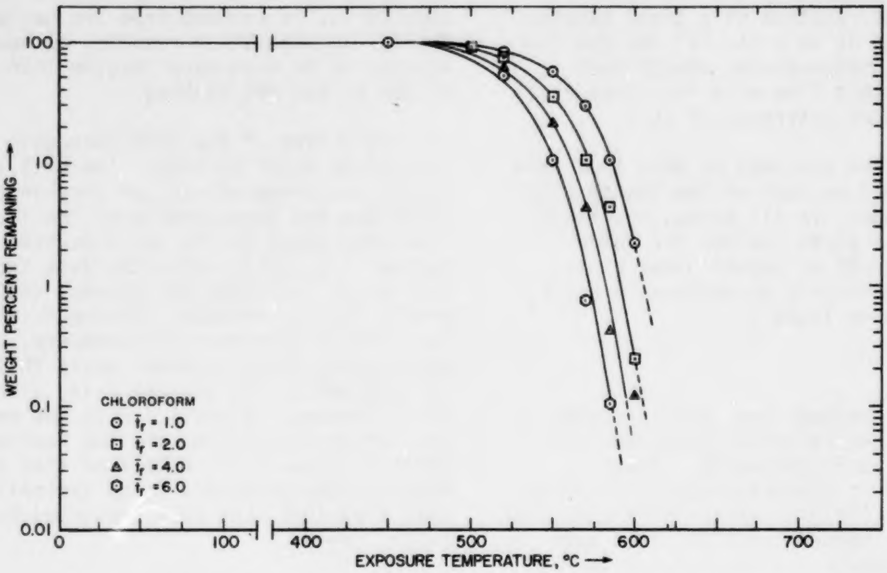

Figure 1. Thermal Decomposition Profiles for Chloroform in Flowing Air at Mean Residence Times of 1.0, 2.0, 4.0, and 6.0 seconds.

predominate, pyrolysis and oxidation.[2]

The global expression for these two reaction schemes are

$$-\frac{d[A]}{dt} = k_1[A]^{\alpha} + k_2[A]^a[O_2]^b. \qquad (1)$$

where: k_1 and k_2 are the global rate constants for pyrolysis and oxidation, repsectively, and α, a, and b, are the reaction order for the decomposition of species A with respect to A and O_2.

The time dependence is included in this expression. The temperature dependence is included in the rate constants for the two processes which may be expressed by the Arrhenius equation:

$$k = A \exp(-E_a/RT) \qquad (2)$$

where: E_a is the activation energy for the process, cal mole^{-1}
A is the Arrhenius coefficient, s^{-1}
R is the universal gas constant, 1.99 cal mole^{-1} °K^{-1}.

For each of the test compounds, it was found that when the thermal decomposition reaction occurred in an atmosphere with a large excess of molecular oxygen relative to the concentration of the waste material, the decomposition equation could be simplified to an expression that is first order in the concentration of the sample. This resulted in the integrated pseudo-first order rate expression:

$$f_r = \exp(-k_2' \; \bar{t}_r) \qquad (3)$$

where: f_r is the fraction of the parent species remaining, and
$k_2' = k_2[O_2]$ is the pseudo-first order rate constant

This expression may be combined with the Arrhenius Equation to yield an expression for the required temperature for a given level of destruction in an atmosphere of flowing air:

$$T_{DE} = 503\, E_a \left[\ln\left(\frac{-\bar{t}_r A}{\ln f_r} \right) \right]^{-1} \qquad (4)$$

where: T_{DE} is the temperature required for a given DE, °K,
E_a has units of kcal mole^{-1} and the other variables are as previously defined.

A plot of ln f_r vs. $\bar{t}_r$ for the four residence times will yield the rate constant for the reaction at a given temperature. A plot of ln k vs. 1/T for the four experimental temperatures should then yield a straight line with the slope equal to $-E_a/R$ and an intercept of ln A.

Regression analyses of this type have been performed on each of the twenty (20) test compounds. In all cases, the first order kinetic plots yielded far better fits than zeroth or second order plots. The measured kinetic parameters, A and E_a, are included in Table 1.

DISCUSSION

Several methods have been proposed for ranking the relative incinerability of hazardous organic compounds. These include heat of combustion per gram molecular weight (Hc/gram of the pure compound) autoignition temperatures (AIT) of pure compounds, theoretical approach based on the kinetics of flame mode thermal decomposition, and gas-phase thermal decomposition of pure organic compounds in flowing air [3-7]. Other parameters can be envisioned which might be appropriate as a basis for such a scale. An attempt was made to correlate laboratory generated gas-phase thermal decomposition data reported in the previous section with the previously proposed rankings scales. This comparison was complicated by lack of overlap of the compounds investigated.

For the heat of combustion scale, the only agreement that could readily be discerned was the general increase in thermal stability with decreasing heat of combustion for the chlorinated benzenes.

There appeared to be a general positive correlation for both $T_{99}(2)$ and $T_{99.99}(2)$ with AIT for those compounds with an AIT below 550°C. Above this temperature the gas phase thermal stability appeared to vary little with AIT.

Direct comparison of thermal decomposition data with the theoretical ranking was hampered by the fact that only four of the 20 compounds were ranked by the group at NBS who developed the approach. However, the thermal stability of the chlorobenzenes ranked by NBS fell in the same order as suggested by the $T_{99.99}(2)$ based ranking. Chloroform was predicted to be rather unstable due to the relatively low energy carbon chlorine bond. This thermal instability is evident from the gas-phase thermal decomposition results, although it appears to be even more fragile than predicted by the NBS ranking.

Only five of the test compounds were studied at Union Carbide. The most significant disagreement was for acrylonitrile which was the least stable of the five compounds based on the Union Carbide calculated $T_{99.99}(2)$, while the data from this study indicates its thermal stability rivals that of methane. Ethane is slightly less stable than monochlorobenzene, as measured by Union Carbide, while this trend is reversed in the present data, although the difference is small. With the exception of acrylonitrile, the two rankings are similar although the data from this study predicts the compounds to be typically more stable by 40°C than that predicted by Union Carbide.

No single proposed ranking scheme or molecular parameter was identified which correlated with all our thermal decomposition data, although trends were observable in homologous subgroups. By careful consideration and utilization of the principles of chemical reactions, it is possible to explain the behavior of each of the twenty compounds on a relative basis and identify possible mechanisms that can be used to extrapolate this limited data to other compounds not studied in the laboratory. The 20 test compounds may be divided into five subclasses; these classes are discussed in the following paragraphs.

Methane, Dichloromethane, Chloroform, and Carbon Tetrachloride

The observed trend in this group is decreasing thermal stability with increasing chlorine substitution, except for carbon tetrachloride which is intermediate in thermal stability between methane and dichloromethane

The data are in agreement with a mechanism based on abstraction of a hydrogen probably by an electrophile. Since the carbon-hydrogen bond dissociation energy (BDE) decreases with increasing chlorine substitution up to chloroform, one would predict decreasing thermal stability, which is observed. However, carbon tetrachloride contains no hydrogens and thus would not be susceptible to this mode of attack. It would instead be expected to decompose by bond rupture.

Benzene, Monochlorobenzene, 1,2-Dichlorobenzene, 1,2,4-Trichlorobenzene, 1,2,3,4-Tetrachlorobenzene, Hexachlorobenzene, Pyridine, Aniline, Nitrobenzene

The observed trend is increasing thermal stability with increasing chlorine substitution. Pyridine is more stable, nitrobenzene is less stable, and aniline has about the same thermal stability as benzene. All of the bonds in benzene, the chlorinated benzenes, and pyridine are probably in excess of 90 kcal/mole and one would expect electrophilic addition to be the predominant reaction path. The chlorines and the nitrogen in pyridine are more electronegative than hydrogen or carbon which leads to a destabilization of the electron deficient intermediate resulting from electrophilic addition, thus reducing the rate of decomposition and greater thermal stability than benzene.

In cases of aniline and nitrobenzene, their stability relative to benzene can also be explained by electrophilic attack. A resonance stabilized intermediate may be envisioned for nitrobenzene, the nitrogen carbon bond dissociation energy (BDE) is 70 kcal/mole which may be easily broken and therefore, represents an alternative mode of decomposition.

Ethane 1,1,1-Trichloroethane, Hexachloroethane

One might expect ethane to be destroyed by unimolecular decomposition through bond rupture at the weakest bond. Due to the 88 kcal/mole carbon-carbon bond one would predict significantly less stability than methane but still moderate thermal stability for ethane.

Although similar in structure, one would expect the pathway for decomposition for 1,1,1-trichloroethane to be concerted elimination of HCl which is a very low energy process [10]. Based on this, one would expect this compound to be one of the least stable compounds studied, which is in fact, the case. Hexachloroethane would have to eliminate Cl_2 to proceed by a concerted pathway. This process is more endothermic and the decomposition of hexachloroethane would instead be expected to proceed through carbon-chlorine or carbon-hydrogen bond rupture, both BDE's being approximately 73 kcal/mole. Based on these considerations, one would expect hexachloroethane to be intermediate in stability between ethane and 1,1,1-trichloroethane, which is the observed trend.

Tetrachloroethylene and Hexachlorobutadiene

Both of these compounds are quite stable. This is probably due to the large BDEs caused by sp^2 hybridization of all carbon atoms and the lack of hydrogen atoms available for abstraction. Electrophilic addition however, may be the predominant mode of attack under incineration conditions. One would then expect hexachlorobutadiene to be thermally less stable since it can form an allyl radical intermediate which is known to be quite stable.

Acetonitrile and Acrylonitrile

These compounds are very stable and all BDEs are 93 kcal/mole or greater. Carbon nitrogen triple bonds are expected to be much less reactive towards electrophilic addition than double bonds. Apparently, the only mode of decomposition for acetonitrile is loss of a hydrogen through bond rupture or abstraction. These are both high energy processes which account for its stability. Acrylonitrile may, on the other hand, be susceptible to addition at the carbon carbon double bond.

CONCLUDING REMARKS

Preliminary calculations indicate that "fault" or "failure" modes of incinerator operation, or equivalently the "extremes" of operational parameter distribution functions, may well control measured incineration efficiency for full-scale units [11,12]. Following this line of reasoning, one would conclude that the incinerator effluent would only contain undecomposed feed material and products of incomplete combustion (PICs) which were formed under these conditions of failure. Thus, "fault" modes are essentially worst case conditions and appear to have a dominating effect on the composition of the incinerator effluent.

A point to be made along this vein is that the temperature at which this study was conducted is probably representative of fault modes. The experimental laboratory temperature range covered 0 to 99.9% destruction of the feed material which is typically several hundred degrees below mean temperatures quoted for hazardous waste incineration. If a given incinerator does not meet the 99.99% destruction efficiency requirement, yet has a high mean operating temperature, then a likely possibility for its failure is that a fraction of the waste feed experiences temperatures somewhat lower than the mean (where destruction efficiency is low) i.e., the destruction efficiency and temperature range measured in laboratory studies.

Thus, one might expect the actual PICs emitted from the incinerator to be the same as those formed under the conditions studied in the laboratory. Furthermore, this reasoning suggests that the relative thermal stability of hazardous wastes should be compared at fault mode temperatures since only this fraction of the waste is escaping incineration. Since selecting a suitable temperature for comparison of every compound is difficult and still somewhat arbitrary, a ranking based on the temperature required for 99% destruction at 2 seconds mean residence time would seem to be a reasonable measure of POHC destructability. One could just as well select 90% or 99.9%, but examination of the data shows that the rankings over this range are essentially identical.

Products of incomplete combustion have not been determined in this study. PIC determination would remove much of the speculation in the discussion of reaction mechanisms. In previous research, the formation of numerous PICs from a wide variety of organic compounds has been observed [13]. These PICs have, in some cases, been produced in as much as 30% yields and been as hazardous or more hazardous than the parent compound. The determination of PICs should be an integral part of future research programs and considered for inclusion in an ultimate ranking of waste incinerability.

The reported research has addressed non-flame, high-temperature, gas-phase reaction chemistry. Extension of this work to include so-called flame mode studies represents a special challenge due to the difficulties in scaling results. Of all incineration processes which must be modeled to full-scale, gas-phase chemical kinetics is the easiest and most successfully performed. The temporal and spatial distributions present in small laboratory or bench-scale flames are not easily scaled to the turbulent poorly-defined flames present in full-scale systems. Consequently, an elementary chemical kinetic approach to determining flame mode destruction efficiencies might prove most effective.

The importance of hydroxyl radicals in flames is well documented [14]. Thus, an experimental program to determine the rate of attack of hydroxyl radicals on hazardous wastes would produce kinetic results which is easily scaled. Kinetic data of this type in combination with measurement or estimation of hydroxyl radical concentrations in full-scale systems would allow simple scaling of laboratory results to full-scale. These data over different temperature ranges would be applicable to both flame and non-flame modes of destruction.

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HAZARDOUS WASTE DESTRUCTION USING PLASMA ARC TECHNOLOGY

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ABSTRACT

A thermal plasma properly applied to toxic and hazardous waste destruction provides a pyrolytic environment with distinct advantages over other competing technologies. Complete atomization of organic fluids have been demonstrated to occur in less than one third of a millisecond. Kinetic recombinations of atomic entities are predictable and generally form acid gas, fuel gas and graphitic soot. Since the process is pyrolytic, the scale of the equipment is small for high throughput rates. Energy requirements for the destruction of organic fluids are typically less than one kilowatt-hour per kilogram of waste. A mobile prototype is being constructed for a throughput rate of four kilograms per minute of liquid organic waste. The mobility and efficiency of such systems may have significant advantages over fixed facilities.

An assessment of approximately forty emerging waste destruction technologies was conducted by the Environmental Protection Agency (EPA). Five were selected for demonstration since they showed a high potential for successful application to toxic and hazardous waste destruction. Under a co-operative agreement between the New York State Department of Environmental Conservation (NYSDEC) and the EPA Industrial Environmental Research Laboratory (IERL) in Cincinnati a demonstration program was established and jointly funded to further investigate mobile plasma pyrolysis. A contract was awarded by NYSDEC to Pyrolysis Systems Incorporated of Welland, Ontario in 1983 for the fabrication and demonstration of the mobile prototype.

The plasma arc device forms the heart of this technology. A co-linear electrode arrangement creates an electric arc which is stabilized by field coil magnets. Low pressure air is used as a medium through which an electric current is passed. In passing through the air, the electrical energy is converted to thermal energy by absorption by the air molecules which are activated into ionized atomic states, losing electrons in the process. Ultraviolet radiation is emitted when the molecules or atoms relax from their highly activated states to lower energy levels.

Waste fluids can be injected into this plasma zone to interact with decaying plasma species to become rapidly atomized prior to exiting this electrode space. An integral part of this process

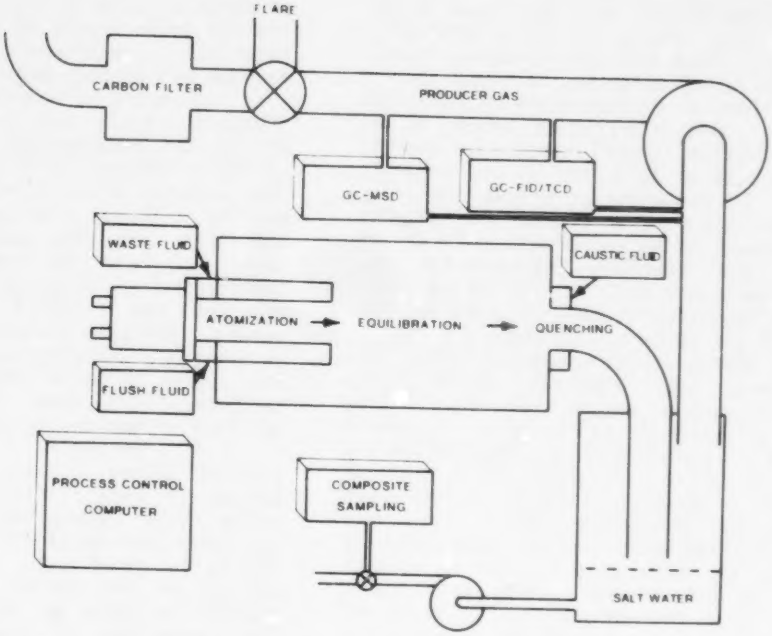
FLARE
CARBON FILTER
PRODUCER GAS
GC-MSD
GC-FID/TCD
WASTE FLUID
CAUSTIC FLUID
ATOMIZATION
EQUILIBRATION
QUENCHING
FLUSH FLUID
PROCESS CONTROL COMPUTER
COMPOSITE SAMPLING
SALT WATER

Figure 1. Process Schematic.

technology is the pyrolytic simulation computer model[2]. New compounds which are created from the recombination of atomic species are predictable based on kinetic equilibrium. The minimization of Gibb's free energy is used to determine the equilibrium concentration of product species over a wide range of selected temperatures and pressures. Thus, appropriate operating conditions can be predicted for any organic waste fluid prior to its destruction. Similarly, undesirable products can be minimized or eliminated through altering the character of the fluid (blending) or the operating conditions. Changes in enthalpy between feedstocks and predicted output products are used to determine the plasma energy required adiabatically for the pyrolysis of the waste being treated.

A simplified process schematic for the mobile prototype is shown in Figure 1. A five hundred kilowatt plasma device is fitted to one end of a stainless steel reaction chamber and mated to a hollow graphite core to form an atomization zone. Residence time in this atomization zone is approximately five hundred microseconds. The reaction chamber serves as the equilibration zone where the atomized species recombine to form new products. This zone is equilibrated at a temperature range of 1200-1800 Kelvin and the residence time in this zone is approximately one second.

A three stage spray ring is located at the producer gas outlet from the plasma reaction chamber. The spray ring is injected with water and appropriate amounts of liquid caustic soda to quench the product gas, neutralize acidic products and trap particulates. Salt water and particulates are pumped from the scrubber sump and sampled prior to approved discharge. An induction fan continuously draws on the reaction chamber and scrubbing system to maintain a slightly negative pressure in the system. Producer gas from the induction fan passes through a three-way valve. During normal operations, this gas flows to the flare stack where it is electrically ignited. Since this gas is mainly hydrogen and carbon monoxide, it burns with a clean flame at a temperature of 2000-2300 Kelvin. This flare stack serves as an air pollution control device to prevent the release of fuel gas to the environment. In the event of a power failure, the three-way valve directs the product gas through an activated carbon filter to block the potential release of undestroyed toxic material to the environment. Provision is made for sampling the product gas prior to the flare.

During normal operation, the plasma pyrolysis unit requires approximately three minutes of warmup time prior to commencing injection of toxic or hazardous wastes. During warmup, the system is injected with a flushing fluid such as ethanol to maintain a reducing atmosphere inside the atomization zone. This unit also requires approximately twenty minutes to cool key components in order to conduct post run maintenance. These short cycle times make this unit basically an on/off system which can respond rapidly to adverse conditions. The system hardware is arranged to provide failsafe operation even in the event of total power failure. Normal scheduled maintenance of pre-engineered components such as fans, motors, valves, meters and sensors should safeguard against unforeseen malfunctions. Thus, consideration for failsafe is limited to monitoring essential conditions and providing protection in the event of an adverse situation.

A MACSYM 350 process control computer is used to control the total operation of the system. The computer provides operator warnings as well as taking positive action in the occurrence of adverse conditions. Under total loss of power, the arrangement of hardware takes over this latter function. Waste feed shutdown signals are triggered by the computer if it senses any loss of the plasma arc, induction system and cooling systems or notes the presence of unacceptable products in the stack product gas. If the arc is lost during toxic waste injection, the response time of the shut off valve may allow as little as five micrograms of undestroyed waste to pass through the pyrolysis system to be trapped on the activated carbon filter. Unacceptable products directed to the carbon filter may include trace levels of principle organic hazardous constituents or excessive release of hydrogen chloride.

In addition to providing waste feed shutdown signals and taking appropriate action, the computer system, through total system monitoring, will also provide operator warning signals which, if not remedied in a preset time period, will automatically shut the system down. Such warning signals stem from monitoring all temperatures, pressures, flows, fluid reserves and standard operating parameters. Failsafe criteria are instituted to safeguard the environment. Obviously, the degree to which the environment is protected will bear directly on the accuracy of monitoring activities.

All hardware is designed to be located within a forty-five foot long moving van type trailer. The hitch end houses the six-pulse, water cooled thyristor unit which is fed with primary 480 volt, three phase power. The rear section of the trailer houses the skid mounted hardware and access is made for the connection of domestic water and sanitary sewer services. The central area of the trailer contains a laboratory in which the control and monitoring equipment are located. In the mobile unit, trace analysis will be performed by a Hewlett-Packard 5792A gas chromotograph coupled to a Hewlett-Packard 5970A mass selective detector (MSD). The MSD has a detection level of one nanogram while in the spectral scan mode and 10 picograms while in the selected ion mode. It is proposed at this time to monitor the product gas before it is flared. Detection of trace chemicals is assisted by their being at their highest molar concentration at that point, where they have yet to be altered through combustion in the flare.

Bulk gas analysis of the scrubbed product gas will also be performed at a sampling point downstream of the induction fan. A Hewlett-Packard 5880A gas chromatograph complete with both flame ionization and thermal conductivity detectors will provide analysis of hydrogen, water, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene, ethane, acetylene, propane, propylene, 1-butene and hydrogen chloride. A detection of 200 parts per million (ppm) of hydrogen chloride in the producer gas will signal a ninety-nine percent removal efficiency of hydrogen chloride in the scrubber during the destruction of wastes containing thirty-five percent chlorine by weight.

It is proposed that this unit be demonstrated in Canada during the summer of 1984. A test program is presently under review by the Canadian Federal and Provincial agencies. Subsequent testing within New York State is contingent upon Federal and State Agency permits.

PROBLEMS ENCOUNTERED

During this project, problem areas have been encountered involving design changes which stemmed from a continuous indepth review process. The as-built schematic for the mobile unit is significantly altered from the proposal originally put forward in the contract. Many of the changes resulted from the selection of alternative hardware. Others were required to improve the failsafe performance. Examples of additional equipment added or equipment modified are the deionized water system, activated carbon filter, air dryer, scrubber water tank, scrubber water pump, plasma field current supply, redundancy in instrumentation and sensors as well as a large selection of valves, piping and wiring to accomodate the requested modifications.

Modifications to the Westinghouse plasma arc system were necessary to ensure that it would provide a similar process performance at an equivalent plasma efficiency. Several weeks of design discussion and testing on a Marc II prototype device and its modified version were conducted to verify the final design. This design was finalized in February, 1984 and the unit is scheduled for delivery in May. The prototype unit achieved destruction efficiencies of 99.9999 percent for askarel solution fed at a rate of 3.6 kilograms per minute[1] on the laboratory reactor at the Royal Military College in Kingston, Ontario. Similarly, parametric data for the modified device show a predictable performance envelop for a rated performance between 200-500 kilowatts. Plasma enthalpies in excess of ten kilowatt-hours per normalized cubic meter were also achieved.

Present guidelines call for monitoring air emissions from the unit. However, it has been shown that the partitioning of toxic compounds passing through the scrubber leaves better than ninety percent of them in the scrubber water. Calibration of the laboratory scale scrubbing unit shows that better than ninety-six percent of low volatile non-soluble (LVNS) compounds are trapped by the scrubber fluid. During typical operation the producer gas and scrubber fluid flowrates are fifteen cubic meters per minute and forty liters per minute respectively. Calculation will show that the LVNS products are more than 69,000 times more concentrated in the scrubber fluid than in the producer gas prior to flaring. These calculations have been verified with parafin oil which is characteristic of most LVNS products of interest (dioxin, etc.). Thus the question of how to measure the performance of this new technology has yet to be resolved. It may be more practical to exercise control over the performance of the system by monitoring for toxic effluents in the scrubber water since it functions on a single pass basis.

RESULTS

The fabrication of the mobile unit should be completed in May 1984. Demonstration testing of the unit is forecast to start in June 1984 and will continue until all regulatory and monitoring concerns have been addressed. Guidelines to assess this technology and the protocols for this assessment are currently under development and should be completed by June.

ACKNOWLEDGEMENTS

Funding for this project has been made possible from the New York State Department of Environmental Conservation and the Environmental Protection Agency Industrial Environmental Research Laboratory. Special recognition is given to Mr. John Grimaud (NASA) for valuable advice in the course of this effort.

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METAL VALUE RECOVERY FROM METAL HYDROXIDE SLUDGES

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ABSTRACT

Metal bearing hydroxide sludge material is generated by the metal finishing industry. This product has traditionally been disposed of in hazardous landfill sites. Long-term maintenance of such sites is required and metal values are unnecessarily lost. The present research effort was initiated to investigate the application of well established hydrometallurgical unit operations to mixed metal bearing hydroxide sludge materials. Test equipment capable of treating 75-100 lbs. per day of mixed metal sludge has been assembled. The test system has been used on a variety of hydroxide sludge materials to demonstrate successful dissolution and selective and effective metal value separation.

INTRODUCTION

In recent years increased emphasis has been placed on preventing the introduction of heavy metal containing industrial wastewaters in publicly owned treatment works and the environment. Legislation has established regulatory authority for controlling the discharge of heavy metals into the environment. It also has mandated resource recovery whenever economically feasible. Many treatment and control technologies have come into existence to remove metals from these wastewaters, i.e., a sludge, concentrate, or regenerate form is created and is, in most cases, disposed of in a landfill. Metals are recoverable, but are not recovered significantly because of a lack of proven technologies.

Process wastewaters from the metal finishing and electroplating industry contain cyanides and heavy metals. These wastewaters have a detrimental effect on the environment if discharged directly. Such discharges are regulated by Federal, State, County, or City ordinances, and require installation of treatment technology. One of the treatment technologies presently in use is oxidation, neutralization and precipitation, which destroys cyanide and removes heavy metals as a hydroxide sludge. This product has traditionally been disposed of in hazardous landfill sites.

Disposal of sludges in landfills has certain inherent disadvantages:

1. Perpetual maintenance of the disposal site is required,
2. Dilution in metal content by mixing with other types of waste materials, and,
3. Permanent loss of non-renewable metals.

If heavy metals are recovered from metal finishing sludges, it will alleviate or reduce the disposal problem and provide for conservation of energy and metal resources. The present study outlines a technical methodology to treat metal bearing sludges by hydrometallurgical techniques.

The treatment of hydroxide sludges for metal value recovery will produce several beneficial results, i.e., economic benefits from the metal values recovered will help offset the cost of recovery/treatment; nonrenewable resource metals will be recycled for use by society; and there will be significantly less hazardous material to be disposed of in landfills.

PURPOSE

The purpose of the present study was to investigate at an advanced laboratory scale the potential for application of well established hydrometallurgical techniques to a mixed metal sludge. The design, development, fabrication, acquisition, and assembly of a treatment system has been conducted at the Montana Tech Foundation Mineral Research Center in Butte, MT.

The objectives of the study included:

- Develop a flowsheet to separate and recover metal values from metal finishing hydroxide sludge materials,
- Develop a test assembly of unit operations to accomplish the separation of metal values on a scale of 75-100 lbs. of sludge per day, and
- Verify that the large scale unit operations accomplish the separation of metal recovery efficiency for each unit operation; delineate process and materials handling problems when treating complex mixed metal sludge materials.

APPROACH

A laboratory test program has been conducted to support the development of an appropriate flowsheet made up of unit operations designed to accomplish the stated objective of separation and metal value recovery from mixed metal hydroxide sludge materials. The laboratory test program was based on a comprehensive review of current literature; discussions with consultative experts in the field of extractive metallurgy; and previous experimental research conducted at Montana Tech Foundation. A flowsheet was designed based on the inputs gained from the above sources and modified as dictated by the laboratory test program.

The flowsheet that resulted from the Phase I study was based on the treatment of a mixed metal sludge material containing significant concentrations of metal values: copper, nickel, zinc, chromium, and variable concentrations of other elements that were not considered recoverable as marketable products but which required removal in order not to contaminate the metal value products, e.g., iron, aluminum, and calcium. The developed flowsheet is not an unalterable sequence of operations; alternatives do exist and will be discussed in the body of this report. As is often the case, unit operations may be accomplished by several different technical approaches, e.g., the unit operation of chromium oxidation may be accomplished by use of chemical oxidation reagents or by use of electrochemical cells. The choice is usually based on efficiency and economical considerations.

Another important point concerning the development of the flowsheet is that only commercial process unit operations and commonly used reagents were considered. That is, new developments in the separation of metals from complex solutions have been reported but are not yet adopted commercially, e.g., iron removal from a mixed metal solution by solvent extraction techniques. These new developments are reviewed in the final project report and the consequences of the adoption into the present flowsheet are discussed.

The flowsheet developed for mixed metal sludges is presented in Figure 1. The treatment sequence consists of the following unit operations:

- Sulfuric acid dissolution of the metal hydroxides.
- Selective precipitation of iron from the solution as a potassium or sodium jarosite ($(KFe_3(OH)_6(SO_4)_2)$.
- Solid-liquid separation of the leach residue and precipitated jarosite solid.
- Selective extraction of copper from the leach solution (with subsequent copper recovery as electrodeposited copper or as crystallized copper sulfate by solvent extraction.
- Extraction of zinc (and residual iron) in preference to chromium and nickel from the leach solution (with subsequent zinc recovery by crystallizing as zinc sulfate) by solvent extraction.
- Selective oxidation of chromium ions to form dichromate anions.

- Selective precipitation of chromium from solution (using lead sulfate) as lead chromate. The lead chromate can subsequently be redissolved to produce a concentrated chromic acid solution with the regeneration of lead sulfate.

- Solid-liquid separation of the precipitated lead chromate.

- Selective precipitation of nickel ions from solution as nickel sulfide or crystallization as $NiSO_4$.

- Solid-liquid separation of the nickel sulfide or $NiSO_4$.

- Recycle of the resulting purified leach solution to the original leach as make-up water. The unrecycled final leach solution may be pretreated by ion exchange before discharge.

Laboratory testwork supports the concept that metal values can be separated and recovered effectively and efficiently from complex mixed metal sludge materials.

RESULTS

The experimental approach and philosophy for the laboratory verification studies include preliminary test of concept by screening experiments; development of a two-level factorial design matrix for the experimental bench-scale studies; execution of the studies in the design matrix to establish which variables are most important and what the relative effect of each particular variable is on the measured result; and subsequent use of the design matrix effects (by using the Box-Wilson "steepest ascent" approach) to optimize the selection of experimental variables for further larger scale testwork.

Large Scale Testwork

The objectives of the large scale test program were: to size the unit operation so that 45.4 kg (100 lbs.) of sludge could be treated per day; to test the unit operations to ascertain if effective and efficient metal value extraction and recovery could be achieved; and to determine what chemical and mechanical problems might be associated with treating approximately 200 liters of leach solution per day.

The test system consists of leach vessels, settlers, a filter press, solvent extraction mixer-settlers, chlorine or electrochemical oxidizer, pH monitors and controllers, precipitating vessels, crystallizers, and an ion exchange column.

A summary of the experimental program and conclusions drawn from the testwork are presented below. The discussion follows the sequence of operations presented in the flowsheet in Figure 1.

The sulfuric acid leach operation is effective in redissolving the metal values (example starting sludge compositions are presented in Table 1). The dissolution is rapid and without control problems. The leach is carried out in a single two hundred seventy liter vessel. The conditions required are well characterized, and rather mild, i.e., one-half hour, 40-50°C, sludge/liquid ratio of 0.8, acid content to control pH in the range 0.5-1.5, and agitation sufficient to suspend the particulate in the solution phase. Example data are presented in Table 2.

The sludge dissolution is essentially complete in less than one-half hour. Therefore, the leach operation is not the controlling step in the overall treatment sequence. The leach unit operation is capable of treating over a ton of sludge per eight hour day. The filterability of the leach residue product is difficult, but may be overcome with the use of filter aids. The filterability of a mixed leach residue-jarosite product is rapid and effective. Therefore, in most testwork the jarosite precipitation process was performed in-situ with the leach residue solids.

The iron removal unit operation is via the precipitation of potassium jarosite. The precipitation process requires elevated temperatures and relatively long reaction times. Two hundred liters of leach solution slurry can be treated in six-eight hours. The jarosite process allows iron to be removed from an acid solution. The product is a crystalline compound that has excellent settling and filtering properties (see Table 3). The iron removal process has been demonstrated on high iron sludge materials, i.e.,

~ 15-20% iron in the starting sludge solids. This means that for these particular sludges a significant quantity of leach residue-jarosite solids is formed, e.g., 11.6 kg of solids or 17.8 kg of wet material. Therefore, the disposal of 17.8 kg would be required instead of 45.4 kg or approximately forty percent of the original sludge weight. A significant quantity of sludge material exists that has iron contents much lower than the above values. The jarosite process is also effective for treating the low iron containing sludges, e.g., two-four percent iron. The quantity of leach residue-jarosite solids produced from such sludge material would be rather small, i.e., a two percent iron bearing sludge would yield 5.6 kg of leach residue-jarosite solid. This quantity of solids translates, at 65% solids, to 8.6 kg of disposable material instead of 45.4 kg or approximately one-fifth the original sludge weight. Jarosites are widely produced in the zinc industry. They are deposited in lined storage ponds. It is difficult to state whether their heavy metal content means that the jarosite should be considered a hazardous material, but even if that is the case at least a significantly smaller weight of material must be considered for disposal.

High iron sludges do (low iron sludges do not) present a problem for chromium recovery. Significant amounts of chromium are lost when the jarosite precipitation is performed. It is believed that the loss can be minimized by maintaining conditions such that chromium is not oxidized and the pH is maintained below 2.5.

Mechanical control of the system is no problem. Chemical control must be exercised to ensure that the pH is maintained in the range 1.8-2.5 and that the iron is in the ferric form. Solid-liquid separation is effectively accomplished by allowing the leach residue-jarosite to settle; decanting the solution from the solids; and pumping the small volume of remaining slurry to a filter press.

The removal of copper is accomplished by solvent extraction (SX) using LIX 622. The extraction of copper from zinc, chromium, nickel, and aluminum is selective and effective (>96% extraction per contact stage). Copper contents of a few mg/liter are achievable in two stages of contact and one stage of strip. The pH of the solution exiting the jarosite precipitation unit operation need not be adjusted prior to copper extraction.

The SX testrack is designed to treat up to 200 liters of solution per day. The design throughput is 500 cc/min. for each phase. Most tests to date have been performed at 250 cc/min. Ten contact mixer-settler units are available for copper SX. Therefore, this unit operation is not the slow step in treatment sequence, i.e., three concurrent streams could be treated (each in three cells) at one time; at 250 cc/min., 360 liters could be treated per day.

Large scale testwork has been conducted for up to six hours. Control of flowrate and interface levels is easily achieved and requires constant attention only during initial loading of the system. Once the system interfaces have been established little operator attention is required. A summary of experimental testwork for large scale continuous testing is presented in Table 4.

The removal of zinc is accomplished by solvent extraction using D_2EHPA. The extraction of zinc from chromium and nickel is selective. Ferric iron, aluminum, and calcium are partially coextracted with the zinc.

The extraction of iron (only between 0.2-0.6 gpl present) with zinc is desirable because it provides a way of removing residual iron from the solution. The iron once extracted into the organic phase is not stripped by H_2SO_4 but is stripped by HCl acid (4-6N). Zinc is stripped by H_2SO_4 (200 gpl). Therefore, a means of bleeding iron from the process stream is to load iron and zinc into the organic phase, strip the zinc by contacting with H_2SO_4 (200 gpl) followed by stripping the iron from the organic by contacting with HCl (4N). Both strip solutions can be recycled until the metal content is appropriate for recovery of zinc as zinc sulfate monohydrate and for disposal of iron as ferric chloride solution.

Calcium is coextracted with zinc but poses no problem because it precipitates as gypsum in the H_2SO_4 strip circuit. It can be effectively filtered continuously from the solution during solution recovery.

Aluminum is co-extracted with zinc and partially stripped in the H_2SO_4 strip circuit. Its presence must be considered during the crystallization of zinc sulfate.

The zinc SX testrack is the same design as used for copper removal. Ten SX cells are available. The removal of 5 gpl zinc requires four stages of extraction, three stages of zinc stripping, and one stage of iron stripping. Therefore, the removal of zinc is the limiting step in the present treatment process. Two hundred liters can be treated at a flow rate of 400 cc/min. for each phase in an eight hour period. Some flexibility does, however, exist by control of the extracting reagent concentration in the organic and by changing the organic to aqueous ratio in the system.

Control of flowrate and interface levels is easily achieved and does not require constant attention once the initial loading and interface levels have been established; i.e., operator attention is minimal. The system can be shut off and restarted without difficulty. Chemical control of pH is required in zinc extraction to achieve effective zinc removal. Solution pH control is exercised by adjusting pH after the first two stages of contact. Temperatures in the range of 40-55°C are desirable for rapid phase disengagement. A summary of experimental testwork for large scale continuous testing is presented in Table 5.

Chromium removal is accomplished by first oxidizing the chromium with chlorine gas, then precipitating the dichromate ion as lead chromate. Oxidation may alternatively be accomplished by use of electrochemical cells. Both systems have been shown to be effective in laboratory scale test reactors. Large scale oxidation testwork using chlorine has been performed successfully; Table 6. Both chlorine oxidation and electrochemical oxidation reactors will be further investigated during Phase II testwork.

A recycle system for stripping the oxidized chromium from the leach solution has been operated successfully: the solution is exposed to lead sulfate in an agitated reactor; lead chromate precipitates; the lead chromate product is crystalline and dense and settles rapidly; the solution essentially free of lead chromate solid is pumped from the solids for further treatment for nickel removal; the lead sulfate solid is separated from the chromic acid and is recycled to the lead chromate precipitation reactor.

Nickel can be removed by sulfide precipitation. The reaction is rapid and near quantitative. The pH is maintained in the range 4-5 so hydrogen sulfide is not released. The solid product is readily filterable. Quantitative removal of nickel is not necessary because practically all the final solution can be recycled to the leach-jarosite precipitation unit operation. Therefore, the addition of a deficiency of sulfide (less than the stoichiometric requirement for complete nickel removal) is desirable so that all the added sulfide ions are consumed. Then when the solution is recycled to the acid leach step, hydrogen sulfide gas will not be formed. An alternative nickel recovery unit operation is nickel sulfate crystallization.

The sequence of unit operations described above results in appropriate metal value recovery from mixed metal sludge materials. Not only are metal values recovered but there is a significant decrease in the quantity of waste material that must be treated for permanent disposal.

ACKNOWLEDGMENTS

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TABLE 1. STARTING SLUDGE MATERIAL BLENDED SAMPLE REPRODUCIBILITY

Composition in Solid (%)								
Cu	Fe	Zn	Cr	Ni	Al	Cd	Cu	Pb
Barrel 5 (used in kettle test)								
2.41	11.33	8.40	1.36	5.08	4.05	0.39	1.08	0.09
2.41	11.88	8.45	1.35	4.08	4.15	0.41	1.00	0.10
2.48	11.65	8.75	1.35	5.08	4.55	0.41	1.10	0.09
2.43±0.05	11.62±0.29	8.53±0.22	1.35±0.01	4.99±0.91	4.25±0.20	0.40±0.01	1.06±0.04	0.09±0.01
Barrel 18 (used in large scale test)								
8.26	19.05	6.15	8.52	1.91	2.66	----	0.31	0.08
6.57	18.06	8.61	7.10	2.23	2.81	0.04	0.45	0.08
6.03	17.37	9.99	6.24	2.28	3.13	0.08	0.44	0.07
4.41	17.16	9.83	4.46	2.45	2.77	0.12	0.64	0.05
4.05	16.91	6.96	4.13	2.47	2.58	0.11	0.64	0.11
5.86±2.36	17.71±1.34	8.31±2.16	6.09±2.43	2.27±0.35	2.79±0.34	0.09±0.03	0.50±0.19	0.08±0.03

TABLE 2. TYPICAL SULFURIC ACID LEACH OF MIXED METAL HYDROXIDE SLUDGE: STANDARD CONDITIONS

	Metal Extracted (%)						
Condition*	Fe	Cu	Zn	Ni	Cr	Cd	Al
100 gm sludge	92.0	93.7	95.9	95.9	96.5	93.0	89.9
650 gm sludge	95.4	94.9	90.5	97.8	96.7	100.0	95.7
1,000 gm sludge	55.8	94.3	94.2	85.0	96.7	97.0	96.0
50,600 gm sludge	92.0	93.7	95.1	95.9	96.5	93.0	96.9

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*Standard Conditions: one-half hour leach; ambient temperature; sludge/liquid ratio = 0.8; acid content equivalent to weight of solids in sludge.

TABLE 3. JAROSITE FILTRATION RATES

	Present Study	Japan*	Canada*
Feed Solids	40-50	50-55	20-30
Solids Loading Rate (kg/m^2/Hr.)	25-55	80-100	40-50
Cake Solids (%)	66-71	78-80	75-78

*Data supplied by Ingersoll-Rand

TABLE 4. SUMMARY OF LARGE SCALE TESTS ON SOLVENT EXTRACTION OF COPPER WITH LIX 622

Condition	Copper extraction from leach solution		
		Copper content in solution	
	Percent	Initial (gpl)	Final (gpl)
Sequential Series One			
Raffinate from contact (40 lit.)	98.9	1.37	0.017
Sequential Series Two			
Raffinate from contact (60 lit.)	94.4	0.39	0.022
Sequential Series Three			
Raffinate from contact (20 lit.)	98.0	2.32	0.047
Sequential Series Four			
Raffinate from contact (90 lit.)	96.9	3.89	0.120
Sequential Series Five			
Raffinate from contact (160 lit.)	99.0	3.05	0.030

TABLE 5. SUMMARY OF LARGE SCALE TESTS ON SOLVENT EXTRACTION OF ZINC WITH D_2EHPA

Condition	Zinc extraction from leach solution		
		Zinc content in solution	
	Percent	Initial (gpl)	Final (gpl)
Sequential Series Three			
Raffinate from contact (20 lit.)	97.4	5.70	0.15
Sequential Series Four			
Raffinate from contact (50 lit.)	97.8	5.89	0.13
Raffinate from contact (90 lit.)	98.8	4.94	0.060
Sequential Series Five			
Raffinate from contact (160 lit.)	98.9	6.20	0.070

TABLE 6. SUMMARY OF LARGE SCALE TESTS ON CHROMIUM PRECIPITATION

Condition	Chromium removed from solution		
		Percent chromium content in solution	
	Per-Cent	Initial (gpl)	Final (gpl)
Sequential Series Four			
Starting solution (10 liters)	---	1.65	---
Final filtrate after 30 min. exposure	99.5	---	0.008
Sequential Series Five			
Starting solution (42 liters)	---	2.34	---
Final filtrate after 30 min. exposure	99.7	---	0.007

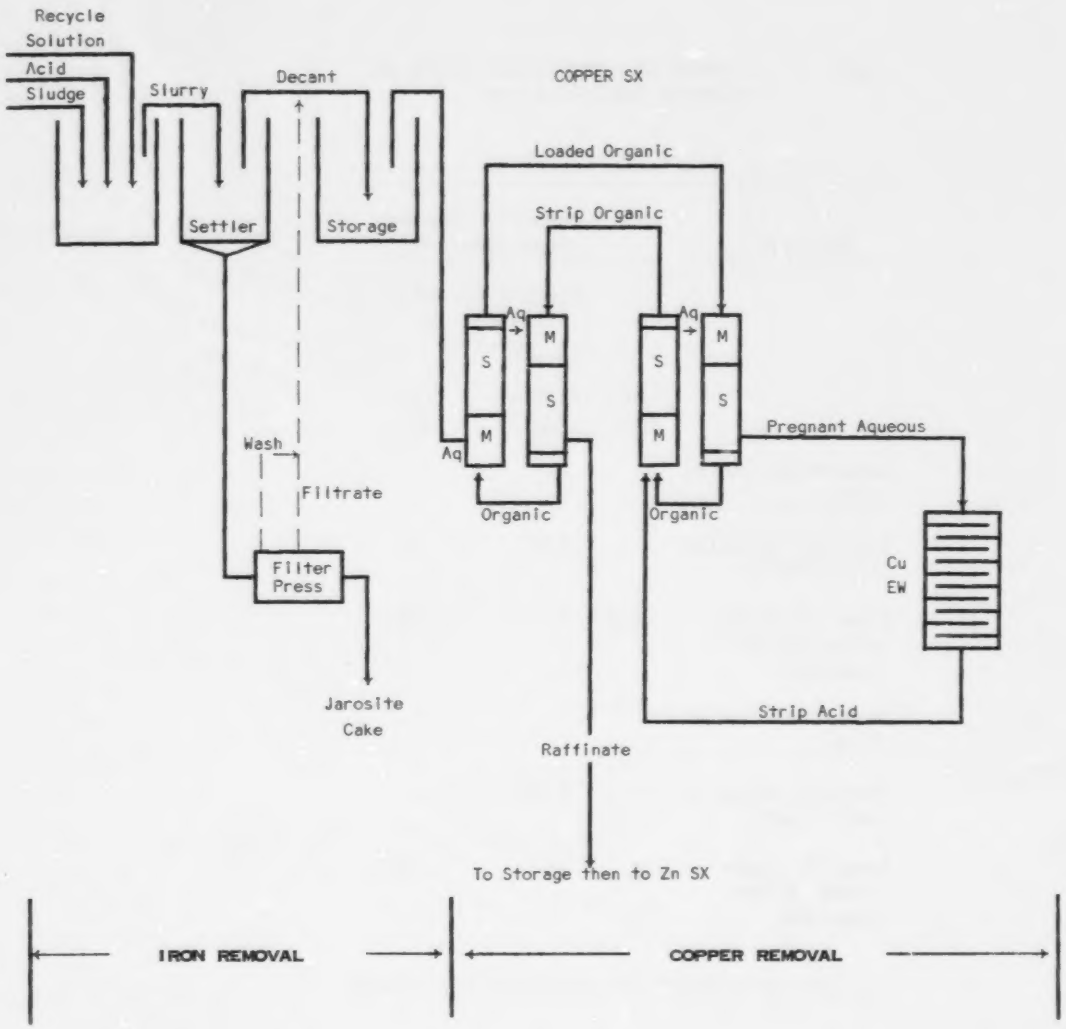
Recycle
Solution
Acid
Sludge
Slurry
Decant
COPPER SX
Settler
Storage
Loaded Organic
Strip Organic
Aq
M
S
Aq
M
S
S
M
S
M
Aq
Pregnant Aqueous
Wash
Filtrate
Organic
Organic
Filter
Press
Cu
EW
Jarosite
Cake
Strip Acid
Raffinate
To Storage then to Zn SX
IRON REMOVAL
COPPER REMOVAL

Figure 1. Flowsheet for Treatment of Mixed Metal Hydroxide Sludges.

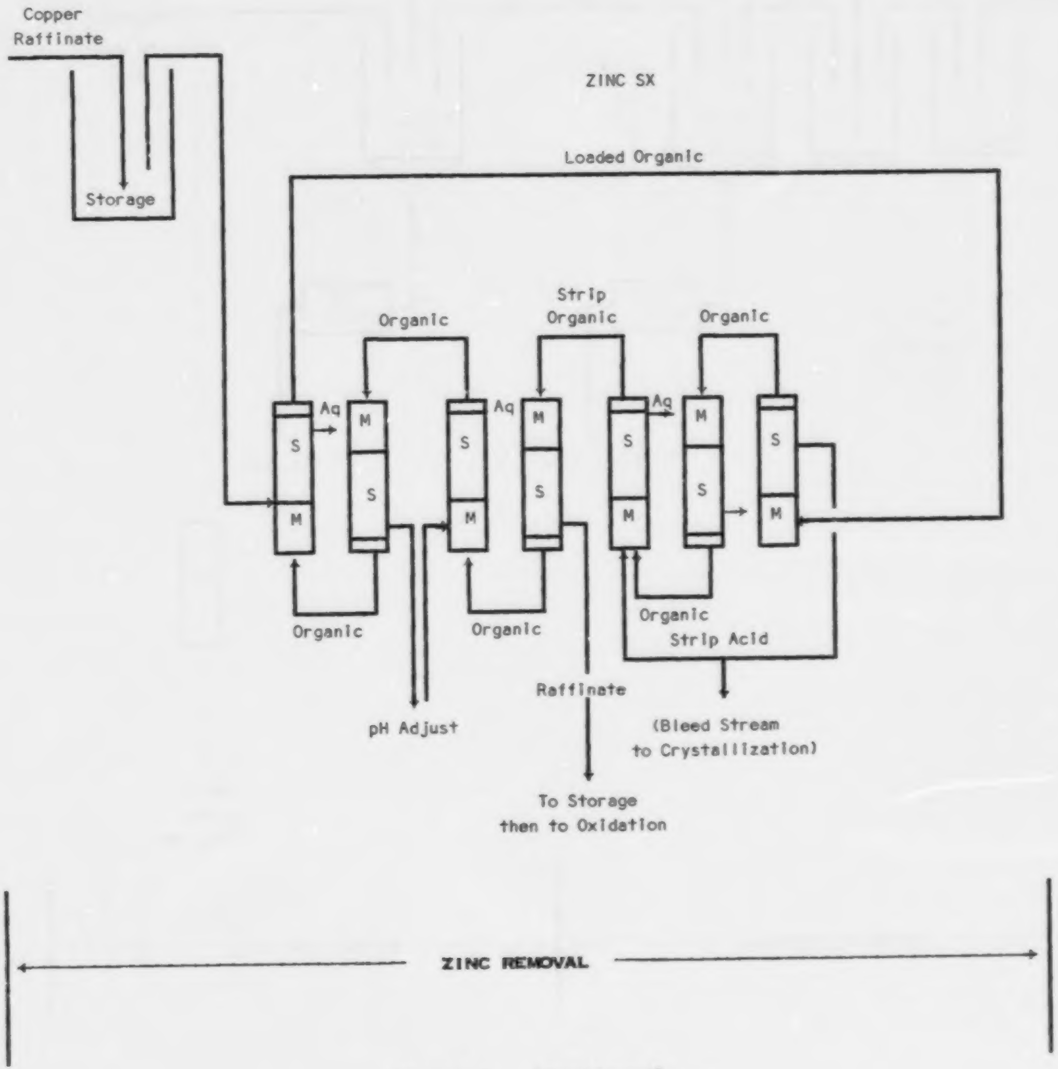
Copper
Raffinate
Storage
ZINC SX
Loaded Organic
Organic
Strip
Organic
Organic
Aq
M
S
S
M
Aq
M
S
S
M
Aq
M
S
S
M
Organic
Organic
Organic
Strip Acid
pH Adjust
Raffinate
(Bleed Stream
to Crystallization)
To Storage
then to Oxidation
ZINC REMOVAL

Figure 1. (Continued).

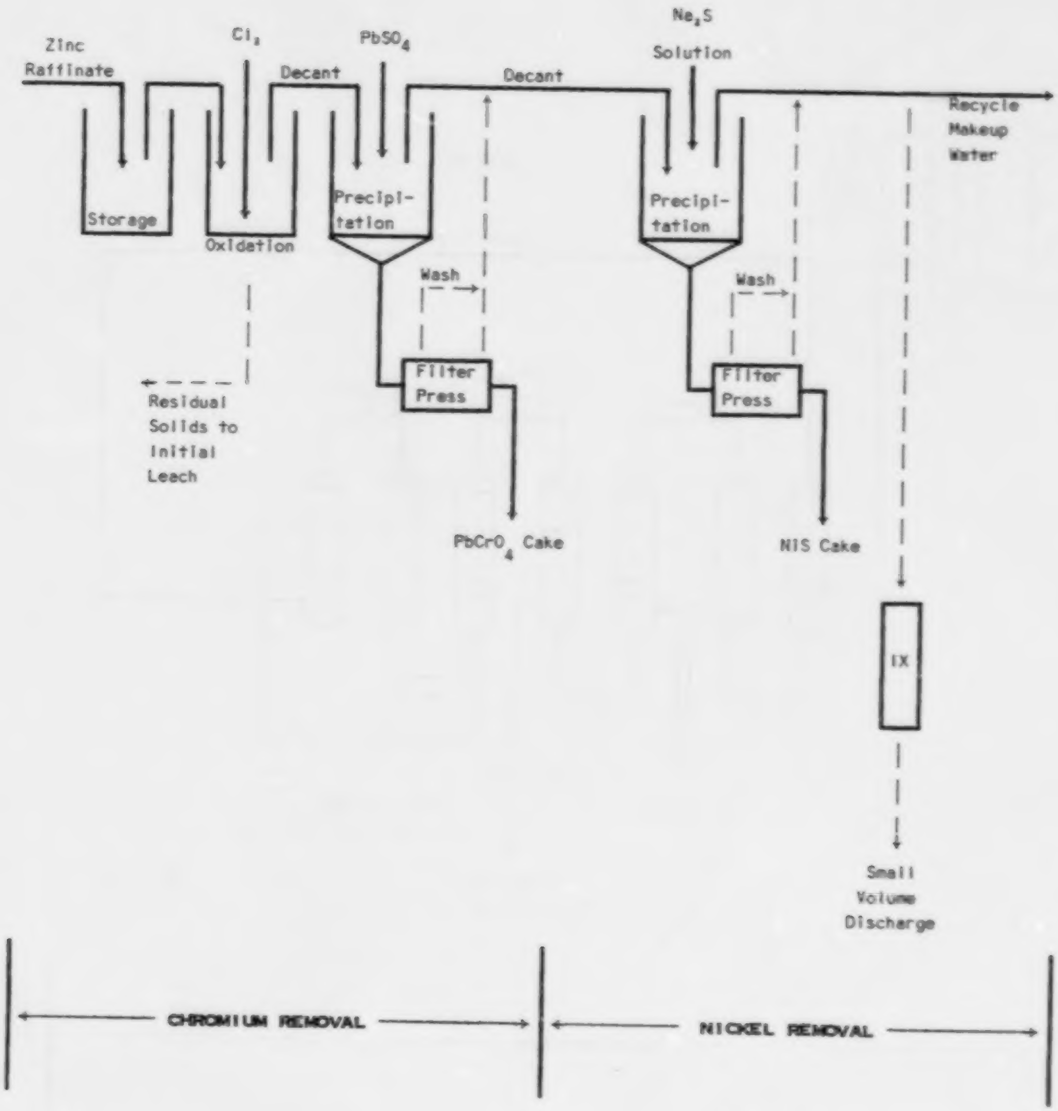
Zinc Raffinate
Cl_2
Decant
$PbSO_4$
Decant
Na_2S Solution
Recycle Makeup Water
Storage
Oxidation
Precipitation
Precipitation
Wash
Wash
Filter Press
Filter Press
Residual Solids to Initial Leach
$PbCrO_4$ Cake
NiS Cake
IX
Small Volume Discharge
CHROMIUM REMOVAL
NICKEL REMOVAL

Figure 1. (Continued).

OPERATIONS AT THE USEPA COMBUSTION RESEARCH FACILITY

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INTRODUCTION

The safe disposal of this Nation's industrial waste is the major goal established by Congress in the Resource Conservation and Recovery Act (RCRA) of 1976. More specifically the USEPA has determined that incineration of those wastes compatible with thermal destruction is the preferred disposal option. Although incineration is the method of choice, its proper implementation and continued safe operation are required before it will be accepted by local citizens or heavily invested in by industrial generators or waste disposal firms. To these ends the USEPA Combustion Research Facility (CRF) has established its mission and goals.

PURPOSE

The CRF has a multi purpose mission in that it will assess the performance capabilities of the rotary kiln/air pollution control device presently installed and will follow these capability analyses to the planned liquid injection unit and its appurtenances when they are fabricated. It will be through performance testing that the CRF will assist in forming the framework of the USEPA policies and regulations regarding thermal destruction of industrial wastes as the disposal route of choice.

The CRF will provide a physical plant for the Agency to test the selection of appropriate Principal Organic Hazardous Constituents (POHCs) for specification in permits and it will directly support the identification of those critical and perhaps lesser known operating variables that contribute to the production of Products of Incomplete Combustion (PICs). The CRF has as an operating purpose the integration of data generated at both the laboratory and bench scale so as to provide the Agency with a potential "incinerability" matrix and identify those waste components associated with thermal environments which should be avoided to prevent the formation of toxic products.

The daily operations at the CRF will provide the Agency and the technical community as a whole a better understanding of the complex thermal processes occurring in an incinerator and the capability to describe the thermal process so as to be able to characterize and assess performance in full-scale systems and to extrapolate performance data from one waste to another or from one technology design scale to another, or even another design itself.

Finally, the CRF will serve as the focal point for the USEPA for definition of compliance monitoring and will provide valuable insights on what must be monitored so proper assurances are given that the incinerator is performing within preselected ranges. The CRF will provide data on sub-system evaluation leading to a total system Destruction and Removal Efficiency (DRE). In this way the CRF will make an invaluable contribution to the national permitting process, the enforcement process, and to citizen acceptance of incineration as an acceptable neighbor.

As can be seen in Table 1, the objectives of the research at the CRF are varied.

TABLE 1. RESEARCH OBJECTIVES OF THE COMBUSTION RESEARCH FACILITY

	Specific Objective					
	1 Process Operating Variable	2 Scaling and Design	3 Reliability & Controlability	4 Destruction of Various Wastes	5 Special Test Burns	6 Components and Subsystem
A - Determine Destruction Mechanisms & Kinetics, Identify PICs (Unregulated Substances)	X		X	X		
B - Engineering Characterization of System Operation	X	X	X			
C - Effects of Waste Feed Constituents & Physical Properties & of Feed System Configuration	X			X		X
D - System Response to Abnormal Operational Modes			X			
E - Permit Compliance Testing	X	X	X	X	X	
F - Determine Destruction Efficiencies for Regulated Waste Materials & Substances	X	X	X	X	X	

PROBLEMS ENCOUNTERED

The conduct of research at the pilot scale is a most difficult task. Being involved in hazardous waste disposal at this scale compounds the difficulty. In the course of events that has transpired at the CRF in getting operations ready to conduct hazardous waste research there are few problems that have not been encountered.

Some problems that caused the largest cost and time increments are

(1) Identification of a properly tested and approved waste container.

(2) Design and procurement of air pollution control equipment standard to the field.

(3) Installation and operation of the on-line combustion gas analysis system.

(4) Preparation of documents for obtaining the necessary EPA permits under RCRA.

FACILITY STATUS

At the present time, the technology that is available at the CRF is a pilot scale rotary kiln with afterburner and an air pollution control system consisting of a variable throat venturi wetted elbow and packed tower scrubber.

The present configuration of the kiln is such that the feed waste is countercurrent to the primary burner. The burner is fitted with an in-line Validyne Engineering Model 11-1-1000 propane meter. The primary combustion air is monitored by an in-line pitot. The kiln temperature is controlled using a shielded thermocouple at the feed face. Additional monitoring equipment on the kiln includes the combustion gases for both composition and flow rate. Combustion gases are monitored for CO, CO_2 and O_2 using an on-line Bendix Combustion Gas Analyzer. The organic components can be determined by extractive sampling using either liquid techniques (EPA Method 5) or solid adsorber sampling systems, such as the Volatile Organic Sampling Train (VOST).

The afterburner temperature is controlled using a shielded thermocouple located at the center point of the chamber. Additional monitoring facilities consist of surface temperature, exit gas temperature, and provisions for determining combustion gas composition and flow rate (essentially the same as are available for the kiln gases).

An Anderson 2000 air pollution control system is fitted to the exit of the afterburner chamber by a refractory line elbow. Here the high temperature gases are contacted with a variable throat wetted venturi operating in the range of 30 inches of water gravity. The gases are cooled and large particulate (if any) is removed. The gases are then passed through a packed spray column and a two stage mist eliminator. Thus far, results show the system performing very well regarding halogen acid neutralization and particulate removal.

The Bendix Combustion Gas Analysis system is utilized to continuously monitor CO, CO_2, and O_2 in the kiln transfer duct, the afterburner and the stack. Temperature is monitored at more than 35 locations throughout the system. These range from routine maintenance temperatures to those in the afterburner and in the stack. Velocity measurements are taken at the head of the kiln and the head of the afterburner. Combustion gas flow measurements ate taken in the kiln exit, afterburner exit and stack as is moisture content and the chlorine and HCl content in each of the three places.

The CRF has in place an approved quality assurance (QA) program that is in complete agreement with all aspects of the required program units. The quality control (QC) aspects of operation also conform to EPA requirements and are an integral part of all analytical operations. A detailed health and safety program has been established at the CRF and is part of daily operations. The general requirements that have been placed on this program are: (a) protection of all personnel who will be responsible for the operation of the facility, (b) protection of the surrounding area, including the community and environment, and (c) protection of the facility and its equipment.

RESULTS

Thus far experiments have been conducted and samples collected during the combustion of propane (background blank), toluene (feedstock for chlorobenzenes), hexachlorobenzene (HCB), and trichlorobenzene (TCB). Table 2 presents the experimental conditions for the experiments.

TABLE 2. HCB AND TCB EXPERIMENTAL TEST SERIES

EXP. NO.	POHC(1) IDENTITY	T_{AB} (°C)	T_k (°C)	FEED RATE (kg/hr)	SAMPLING POSITIONS(2)	REMARKS
1.	Propane	1093	879	~59	(a),(b)	Background
2.	Propane Toluene	1093	871	~59 2.43	(a),(b)	Background
3.	Propane Toluene	982	871	~56 2.43	(a),(b) (a),(b)	Background
4.	Propane Toluene	871	760	~50 2.43	(a),(b) (a),(b)	Background
5.	Propane Toluene	871	760	~48 2.43	(a),(b)	Failure Mode-AB burner shut off 2 min. every 15 min.
6.	Propane Toluene HCB	1093	871	~59 2.43 0.10	(c)	HCB fed as solution in Toluene
7.	Propane Toluene HCB	982	760	~56 2.43 0.10	(c)	HCB fed as solution in Toluene
8.	Propane Toluene HCB	810	760	~46 2.43 0.10	(c)	HCB fed as solution in Toluene
9.	Propane Toluene 1,2,4-TCB	1093	871	~59 2.43 0.10	(c)	1,2,4-TCB fed as solution in toluene

(continued)

TABLE 2 (continued)

EXP. NO.	POHC(1) IDENTITY	T_{AB} (°C)	T_k (°C)	FEED RATE (kg/hr)	SAMPLING POSITIONS(2)	REMARKS
10.	Propane Toluene 1,2,4-TCB	1093	871	∼59 2.43 0.25	(c)	1,2,4-TCB fed as solution in toluene
11.	Propane Toluene 1,2,4-TCB	1093	871	∼59 2.43 0.5	(c)	1,2,4-TCB fed as solution in toluene
12.	Propane Toluene 1,2,4-TCB	1093	871	∼59 2.43 1.00	(c)	1,2,4-TCB fed as solution in toluene
13.	Propane Toluene 1,2,4-TCB	1093	871	∼59 2.43 0.10	(a),(b)	1,2,4-TCB fed as solution in toluene
14.	Propane Toluene 1,2,4-TCB	982	871	∼56 2.43 0.10	(a),(b)	1,2,4-TCB fed as solution in toluene
15.	Propane Toluene 1,2,4-TCB	871	982	∼50 2.43 0.10	(a),(b)	1,2,4-TCB fed as solution in toluene
16.	Propane Toluene 1,2,4-TCB	871	982	∼48 2.43 0.10	(a),(b) (a),(b)	Failure mode as above in Experiment 5
17.	Propane 1,2,4-TCB	1121	788 to 760	∼46 4.0	(a),(b)	Failure mode in kiln
18.	Propane 1,2,4-TCB	1121	732 to 704	∼46	(a),(b)	Failure mode in kiln
19.	Propane 1,2,4-TCB	1121	677 to 649	∼46 4.0	(a),(b)	Failure mode in kiln

(1) Chemical(s) fed to simulate Principal Organic Hazardous Constituent (POHC).
(2) Position (a) = kiln transfer duct; (b) is AB transfer duct; (c) is stack.

Selected DRE's for the experiments using the chlorobenzenes are presented in Table 3.

TABLE 3. RESULTS OF SELECTED CHLOROBENZENE EXPERIMENTS

Exp. No.	T_{AB} (°C)	T_k (°C)	Feed Rate (kg/hr)	Emission Rate (gm/hr)	DRE %
8	810	760	0.1	2.23×10^{-3} 2.03×10^{-3}	99.998 99.998
7	982	760	0.1	4.41×10^{-3} 3.47×10^{-3}	99.996 99.997
6	1093	871	0.1	1.66×10^{-3} 0.50×10^{-3}	99.998 99.999
9	1093	871	0.1 0.25	0.31×10^{-3} 0.25×10^{-3}	99.9997 99.9999
10	1093	871	0.5	0.67×10^{-3} 0.86×10^{-3}	99.9998 99.9998
11	1093	871	1.0	1.90×10^{-3} 2.74×10^{-3}	99.9998 99.9997
				TOTAL EMISSION	DE%+
17	1121	788-760	*	104.6 μg	99.9991
18	1121	732-704	*	342.3 μg	99.992
19	1121	677-649	*	0.305 grams	97.2

+ DE = Destruction Efficiency as opposed to DRE.

* The 1,2,4-trichlorobenzene was fed at a rate of 66.7 gm per minute for an elapsed time of 30 seconds. Thus a total of 33.35 gms was fed in each of the experiments. Assuming that all feed was volatilized and removed from the kiln during this time, and taking the appropriate (measured) flow rate for each of the conditions, we compute DE as follows:

$$DE = 1 - \frac{C}{C_0}$$

where $C_0 = \dfrac{33.35}{\text{kiln flow}}$ and would be the concentration in the kiln flue gas if DE=0.

Kiln flow for experiment 17=5.70 (DSCMM), 18=6.28 (DSCMM), 19=6.02 (DSCMM)

In addition to the aforementioned sequence of experiments, the ability to accurately determine flow rates and specific concentrations of combustion products allows an estimate of the heat release from the stoichiometric equations for the oxidation of propane:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

Researchers at the CRF have compared the total heat release against four (4) methods of measurement. The results of these measurements are presented in Table 4.

TABLE 4. COMPARISON OF HEAT RELEASE (MMBtu/hr.)

Heat Release From Stack Gas Analysis		Heat Release Based On Inline Gas Meters	Heat Release Based on Combustion Gases and Surfaces Losses
CO_2	H_2O	Propane Flow	
1.94	1.87	1.97	1.97

The excellent agreement between the various estimates of the heat release lends credence to the various measurement techniques used.

FUTURE OF CRF

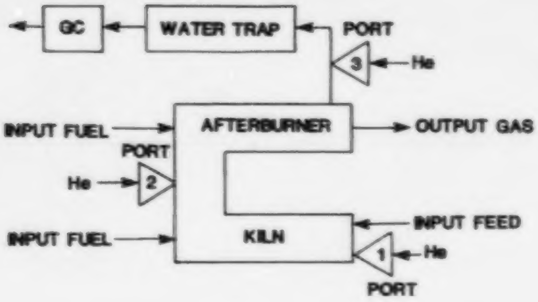
Presently the CRF is anticipating receipt of a final Part B RCRA incinerator permit to be issued by the State of Arkansas under Phase II authority granted by the USEPA. Until such a permit is received operations at the CRF shall be limited to commercially available chemicals and synthetic mixes. Once permission is received the CRF is geared to secure several candidate waste streams for active investigation.

Research shall be directed toward a better understanding of residence time. It has often been said that the operation of an incinerator is governed by the three T's - time, temperature and turbulence. The Time spent (its residence time) in an afterburner is normally determined by the prescription, Equation (1).

$$t_r = \frac{V}{Q} \tag{1}$$

where V is the chamber volume and Q the throughput of combustion gases measured at the exit temperature of the chamber. There are several problems with this. The gas temperature within the chamber can be expected to be significantly above that at the exit and therefore to move the same mass of gas through the unit area requires a higher velocity. Also, the turbulence within the chamber must result in not all elements of the combustion gas remaining within the chamber for the same time period. For these reasons the CRF is presently undertaking a detailed investigation to define t_r as some sort of average time within the high temperature chamber. It was recognized that helium dilution could be used for an actual measurement of residence time in addition to the above mentioned utility for high temperature flow measurements. Instead of a steady input flow as required by the former measurement, a measure of the time of arrival of helium introduced as a sharp pulse will then allow a measurement of the residence time within the chamber. Preliminary results of the residence time distribution measurements have been very exciting and it is anticipated that these experiments will be completed in the near future. Figure 1 is a schematic of where helium will be introduced in the system and where analysis will occur.

FIGURE 1



The concept of hot zone sampling has been investigated by others but not to the extent as called for at the CRF. At the present time there is a stationary probe located in the transfer line from the kiln to the afterburner and in the duct from the afterburner to the scrubber. These probes are in zones that are non-laminar in flow so that mixing might be induced and thus concentration uniformity of chemical species would occur. There is no attempt to sample iso-kinetically. At the present time samples are being collected using the solid absorbents XAD-2 and Tenax in which further sample manipulation follows in the laboratory. Results of these efforts will be forthcoming in separate CRF documents, some of which will be submitted to referred journals.

Other areas in which the CRF is conducting investigations are:

- Chlorine balance in the scrubber water
- Fixed vs Traversing sampling in the stack
- Flame out failure mode experiments
- Sub-system destruction/removal efficiency calculations
- Product(s) of incomplete combustion analysis and prediction of species
- Correlation of pilot scale data to lab and bench scale results
- Evaluation of modified solid absorbent clean-up procedures.

In the future several reports and journal publications will transmit the results and significance of these and other studies at the CRF.

In an attempt to assure that there exists a high degree of coordination between the several IERL incineration research programs it has been determined that each should study several of the synthetic waste streams referred to as EPA "Soups." This approach has been taken to obviate the variations that can be expected in actual industrial wastes and is expected to yield data that will allow direct intercomparison among the several programs. This procedure, in addition to generating information of direct value itself, should also assist in understanding the means by which laboratory data should be extrapolated to pilot and full scale technology. The protocol which is herein presented is designed to extract the maximum of information from a series of incineration tests at the CRF on the first of these soups.

The experiments described below are anticipated to yield data directly applicable to the following:

- A determination of the effects of afterburner temperature, residence time and excess air on the thermal stability of the compounds that make up the EPA soup #1
- The effect of kiln conditions on the DE of the afterburner
- The effect of kiln conditions on the production of PICs from the soup feed
- The effect of feed rate of the soup on both DRE for the components of the soup and on the production and stability of PICs
- The effect of variations of RTD on the observed DRE for the afterburner
- Development of thermal stability data that will allow comparison to other technologies
- Investigation of scrubber holdup effects
- Obtain operational experience on the use of the VOST system for sampling and analysis of POHCs (and PICs) which are suitable for purge and trap analytical methods.

The philosophy that has underlain the CRF operations from the beginning of the program has been that all experiments should be conducted from a technically conservative viewpoint. That is to say, every effort should be expended to design experiments that would yield useful data while at the same time conducting the tests so as to have minimal impact on the facility and the immediate environment. This attitude will be considerably impacted when the HEPA/carbon filtration system is in place since use of the system will always ensure that emissions are within permissible limits. The experimental protocol suggested for the soup experiments is presently dictated by this conservative attitude which requires beginning with low feed concentrations and maximum thermal conditions within the incinerator. As it is shown that no more than permissible emissions are found under these severe conditions the conservative restrictions are gradually relaxed. At each step the emission levels determine the advisability of proceeding to the next less severe operations set. This process continues until either the entire set of experimental conditions has been explored or until a set of operational parameters has been attained for which non-permitted conditions are found.

The proposed set of test conditions will be carried out using the EPA soup as indicated below:

Soup components:

carbon tetrachloride (CCl_4);
trichloroethylene ($C_2H_3Cl_3$);
monochlorobenzene (C_6H_5Cl); and
Freon 113 ($C_2Cl_3F_3$) in a
toluene matrix.

It is proposed that several solutions be made up of this combination as follows:

Feed Mix B_1 (in the proportions as follows)

C_6H_5Cl	93.5 ml	corresponding to 31.5 gm Cl_2
$C_2H_3Cl_3$	68.0 ml	corresponding to 58.0 gm Cl_2
CCl_4	62.7 ml	corresponding to 92.2 Cl_2
$C_2Cl_3F_3$	66.0 ml	corresponding to 37.4 gm Cl_2 + 30.4 gm F_2
C_7H_8	2500.0 ml	
TOTALS	2.79 liters	containing 219.1 gm Cl_2 + 30.4 gm F_2

Feed Mix B_2 (in the proportions as follows)

C_6H_5Cl	467.5 ml	corresponding to 157.5 gm Cl_2
$C_2H_3Cl_3$	340.0 ml	corresponding to 290.0 gm Cl_2
CCl_4	313.5 ml	corresponding to 461.0 gm Cl_2
$C_2Cl_3F_3$	330.0 ml	corresponding to 187.0 gm Cl_2 + 152 gm F_2
C_7H_8	1349.0 ml	
TOTALS	2.80 liters	containing 1095.5 gm Cl_2 + 152 gm F_2

It is noted that Mix B_1 has a heating value of 114 MBtu/gal whereas Mix B_2 has a heating value of approximately 62 MBtu/gal.

The feed rates to be used for both Mixes B_1 and B_2 will be 2.84 l/hr (0.75 gal/hr).

The actual proposed experimental matrix is shown in Table 5.

TABLE 5. EPA SOUP - EXPERIMENTAL MATRIX

Experiment	T_K (°F)	T_A (°F)	Feed	Sampling*			
				K	A	Stack	Blowdown
A_1	1600	2100	B_1	4	2	2	1
A_2	1400	1800	B_1	4	2	2	1
A_3	1200	1600	B_1	4	2	2	1
A_4	1200	1400	B_1	4	2	2	1
A_5	1600	2100	B_2	4	2	2	1
A_6	1400	1800	B_2	4	2	2	1
A_7	1200	1600	B_2	4	2	2	1
A_8	1200	1400	B_2	4	2	2	1
A_9	1400	2000	B_2	2	2	2	1
A_{10}	1400	2000	B_2	4	2	2	1

*Integer refers to the number of samples to be taken.

Experiments A_9 and A_{10} will be failure mode experiments. In experiment A_9 the afterburner propane feed will be shut off for 2 minutes out of every 15 minutes. A_{10} will involve the same procedure for the kiln burner.

In the event that the high concentration feed stock, B_2, shows compliance under all conditions, it will be appropriate to conduct an additional series of experiments using Mix B_2 but at a feed rate of 5.6 l/hr (1.5 ga/hr) at conditions similar to A_5 and A_6.

In all cases (sets of parameters in Table 1) the kiln residual pressure will be adjusted to -0.05 inches of water, gauge, in order to keep the excess air approximately constant.

CONCLUSIONS

The following conclusions may be drawn from recent studies on the incineration characteristics of selected chlorinated benzenes in toluene solution:

- The CRF incinerator can produce the required DRE of greater than 99.99% for the selected POHCs.
- The procedures for hot zone sampling that have been implemented appear to yield consistent results.
- Comparison of absolute quantities of several chlorinated benzenes to soot weight in kiln samples shows no correlation.
- The behavior of the afterburner at low injection rates is apparently dependent on the presence of PICs that are derived from the POHC.
- There is apparently a direct relationship between DE_A and the injection rate at low injection rates.
- As expected, the existence of a residence time distribution in the afterburner results in the failure of first order kinetics to describe the destruction of hexachlorobenzene and 1,2,4-trichlorobenzene.
- The proposed residence time distribution and the method of its measurement apply quite well to the CRF incinerator.
- The use of helium dilution for the measurement of combustion gas flow yields consistent results.
- There apparently exists a strong interrelationship between 1,2,4-TCB pentachlorobenzene and HCB, a relationship suggesting that any two will be PICs derived from the third.
- The proposed scrubber blowdown model appears to be directly applicable to the CRF incinerator.
- The poor turndown of the Iron Fireman burners limits the feed rate that can be used, indicating the need to replace these burners.
- The castable refractory has stood up remarkably well even under the severe thermal stress of intermittent operation. Engineering tests conducted without POHC feed always show the POHC and PIC from previous analytical tests which were conducted with POHC feed.

RECOMMENDATIONS

- The successful demonstration of a method of residence time distribution measurement in the CRF afterburner opens the door to an online measurement of retention time which could then become a monitoring and control method.

- The successful application of simple models to such aspects of the CRF incinerator as the afterburner retention time and the blowdown discharge suggest that modeling of other aspects of the system can lead to enhanced understanding of the incineration process and to better control thereof.
- Attempts should be made to allow the measurement of mixing in the afterburner and the effects of such mixing on the temperature distribution as well as on the retention time distribution and thereby on the performance of the incinerator.
- The fact that a new feed face configuration has been designed with the capability of pumpable fluids, solids and containerized solids feed indicates that by the time the RCRA permit has been issued, the CRF will be in position to study complex or problem wastes.

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SAMPLING METHODS FOR EMISSIONS FROM HAZARDOUS WASTE COMBUSTION

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ABSTRACT

Incineration as a means of hazardous waste disposal has received increasing attention during the last several years. Since it is necessary to characterize the stack emissions as well as the waste in order to determine how well the unit is operating, research into adequate methods of sampling and analysis has been necessary. This paper presents an overview of the sampling methods which are resulting from current and previous research programs and which are being recommended to EPA regulatory programs to EPA engineering research and development projects, and to interested parties in the industrial community. The methods discussed are generally applicable to incineration and also to processes closely related to incineration, such as co-firing of waste in industrial boilers, and burning of contaminated heating oil.

Although methods for inorganic hazardous compounds are very briefly outlined, the primary emphasis of the paper is on organic compounds which are likely to be chosen as principal organic hazardous constituents (POHCs) for a trial burn. Methods receiving major attention in this paper include: the Modified Method Five Train (MM5) which includes an XAD-2 sorbent module, the Source Assessment Sampling System (SASS), the recently developed Volatile Organic Sampling Train (VOST), and assorted containers such as glass bulbs and plastic bags.

INTRODUCTION

Incineration as a means of hazardous waste disposal, especially for organic materials, has received increasing attention during the last several years. Although there are many measurements that may be made in order to characterize the operation of an incinerator, virtually all of them require sampling and analysis of the flue gas as well as the waste feed material. Although sampling and analysis of incinerator emissions have been accomplished in the past, a number of advances in the state of the art have been made within the last few years. The range of chemical compounds likely to be of interest has also widened considerably.

A program to provide and document adequate methods for characterization of hazardous waste incinerators is being carried out by EPA's Office of Research and Development (ORD). A reference document(1) for use by ORD incineration engineering R&D programs, EPA's Office of Solid Waste and Regional Offices, and the regulated community has been released, following peer and policy review. The methods in Reference 1 are state of the art, and are scientifically sound. Extensive programs of careful and thorough validation, which are underway at present, will greatly benefit the users of these methods. In the meantime, the methods to be described are best used by those with considerable experience in stack testing and chemical analysis: as much expert advice as possible should be sought when preparing or carrying out an incineration characterization project.

This paper presents an overview of the methods proposed in Reference 1 with special emphasis on stack sampling of organic compounds likely to be chosen as principal organic hazardous constituents (POHCs).

Stack Sampling Methods

Although numerous sampling methods might be applied to a given incinerator, this discussion will concentrate on four approaches that are being utilized to the greatest extent, not only because of their generally high performance, but because of their flexibility and usefulness for a wide range of materials.

The Source Assessment Sampling System (SASS), Figure 1, was developed for environmental assessment programs and is still the train of choice when large amounts of samples are necessary for extended chemical analysis or biotesting. The SASS includes: cyclones for particle sizing, a glass or quartz fiber filter for fine particle collection, a sorbent module for collection of semivolatile organics, and impingers for collection of volatile metals. The SASS operates at 110 to 140 Lpm (4 to 5 cfm) and is usually operated long enough to collect 30 m^3 of flue gas. It is possible, but not convenient, to traverse a stack with an SASS, so it is usually operated at a single point in the stack under pseudo-isokinetic conditions. For further details as to the meaning and potential ramifications of this mode of sampling, see Reference 2.

Potential corrosion of stainless steel in the sorbent module of the SASS has prompted development of glass sorbent modules which appear to perform adequately. One of these is described in Reference 3.

The Modified Method Five Train (MM5) is conceptually very similar to the SASS but operates at a lower flow rate, usually 14 to 28 Lpm (0.5 to 1 cfm). The MM5, shown in Figure 2, does not include particle sizing cyclones, and is usually constructed of glass rather than stainless steel. The MM5 results from a very simple modification of any of the commercial sampling trains available which conform to the requirements of EPA Method 5. The sorbent module with cooling capability is simply inserted between the filter and the first impinger. The sorbent module must be positioned vertically so the gas and any condensed liquids flow downward through it.

The sorbent of choice for most sampling jobs for both the SASS and MM5 is XAD-2. For further discussion of the reasons behind this choice, as well as sorbent module placement in the train see Reference 2.

Because of its more convenient size and ready availability, the MM5 is usually chosen over the SASS for incinerator sampling unless larger samples are needed for lower detection limits or extensive analysis requirements.

Either the SASS or MM5 provides collection ability for particulate material, acid gases such as HCl, gaseous metal compounds (if appropriate collection liquids are chosen), medium boiling organics (b.p. 100°C to 300°C), and high boiling organics (b.p. greater than 300°C). Organics with boiling points between 100°C and 120°C require individual attention during the sampling planning stage and may require decreased sampling times to prevent volumetric breakthrough. Volumetric breakthrough is related to the migration rate of sorbed material through unsaturated sorbent beds. For further discussion of this important concept, see Reference 2.

Considerable field experience has been gained with the SASS and MM5 trains even though formal validation procedures have not been completed. Much of the confidence in these trains' ability to collect organics rests on knowledge of the behavior of sorbents with respect to collection and recovery. Reference 2 discusses this point in more detail. A particularly effective demonstration of these trains' performance on a dioxin injected into combustion gas is given in Reference 4. Similar research with other compounds is underway, and a validation project has begun.

The MM5 and SASS are not generally quantitative collection trains for organics with b.p. less than 100°C. For these low boiling compounds, the recommended methods are plastic sampling bags, glass sampling bulbs, or the newly developed volatile organic sampling train (VOST). The ambient air at many incinerator sites exhibits relatively high levels of volatile organics. This greatly increases the difficulty of obtaining an uncontaminated sample of low concentration and requires a great deal of care as well as adequate blanks. All of the above methods have shortcomings, but they are much less severe than the shortcomings and limitations of alternate approaches (2).

The VOST is shown in Figure 3. This train and the analysis approach applied to the samples resulting from its use were developed in order to address stack concentrations as low as 0.1 ng/L. A sorbent tube containing 1.6 g of Tenax is positioned early in the train in order to remove organics from the gas and liquid stream as soon as possible. A second sorbent tube containing 1 g of Tenax and 1 g of charcoal follows the condensate collector in order to act as a backup in case of breakthrough. The charcoal provides added stopping power for the very low boilers such as vinyl chloride. The train was designed to use six pairs of sorbent tubes sequentially, each operating for 20 minutes at 1 L/min. The ability to concentrate the organics from all six sets of tubes onto one analytical tube and subsequently heat desorb into a GC or GC/MS makes it possible to achieve very low levels relative to the stack gas concentration. For higher stack gas concentrations, it appears to be possible (perhaps even necessary) to operate the VOST at lower flow rates and longer sampling times. There is no fundamental reason why this piece of equipment should not be useful in a number of operation modes as long as excessive volumes of gas are not pulled through a single tube, since low boilers break through the sorbent after relatively low volumes.

The development and use of the VOST has been discussed in several publications(5,6, 7). Reference 7 is particularly useful to users of the train. Preliminary evidence that the train is effective is given in these references, and an EPA validation project for the VOST is underway.

Various types of plastic sampling bags have been used in the past, with very mixed results. It is quite possible to get good results with this approach, but it is essential that the sampling and storage characteristics of the specific POHC, relative to the specific types of bags to be used, be well known. For example, organics such as alcohols usually exhibit poor storage characteristics in bags (8). It is also essential that field blanks be included in the sampling strategy, since all known methods for volatile organics from incinerators are subject to potentially severe contamination in the field and during transit.

When sampling relatively high concentrations of volatiles, glass sampling bulbs with secure seals may be the best choice. Although somewhat inconvenient and lacking in sample concentrating ability, the glass bulbs do show better sample storage characteristics than plastic bags (8).

In addition to the methods discussed, special procedures may be necessary for certain pollutants. Formaldehyde is an example of compounds that require special handling (9). Reference 1 gives guidance in such cases. A number of other less satisfactory general sampling approaches exist, but have not been recommended. For further discussion of these techniques and their shortcomings, see Reference 2.

Summary

Sampling methods have been discussed which are generally applicable to incineration and to processes closely related to incineration, such as cofiring of waste in industrial boilers, and burning of contaminated heating oil. Although some of the methods are relatively new and all require a great deal of care and attention, it is possible to produce excellent results through their application.

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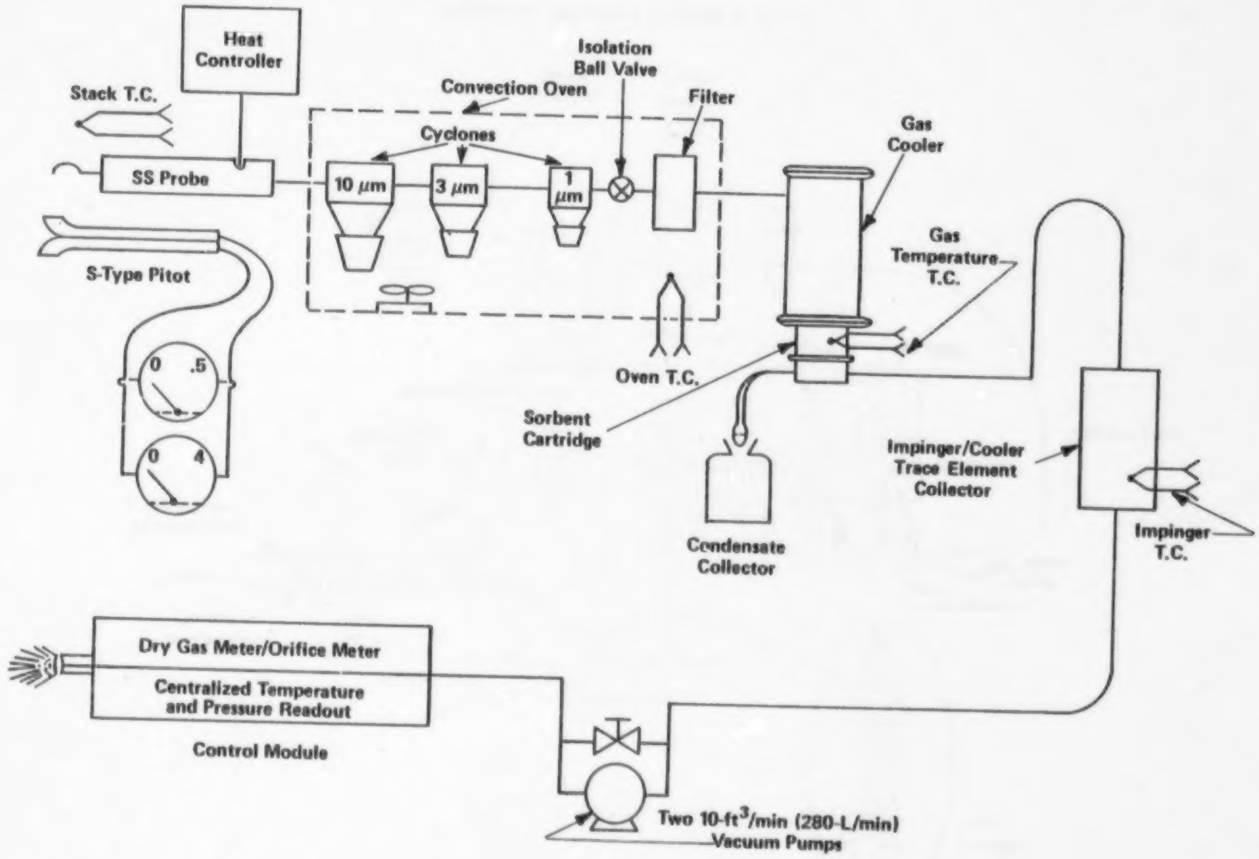
Heat Controller
Stack T.C.
SS Probe
S-Type Pitot
0
.5
0
4
Convection Oven
Cyclones
10 μm
3 μm
1 μm
Isolation Ball Valve
Filter
Oven T.C.
Sorbent Cartridge
Gas Cooler
Gas Temperature T.C.
Condensate Collector
Impinger/Cooler Trace Element Collector
Impinger T.C.
Dry Gas Meter/Orifice Meter
Centralized Temperature and Pressure Readout
Control Module
Two 10-ft³/min (280-L/min) Vacuum Pumps

Figure 1. Source assessment sampling system (SASS).

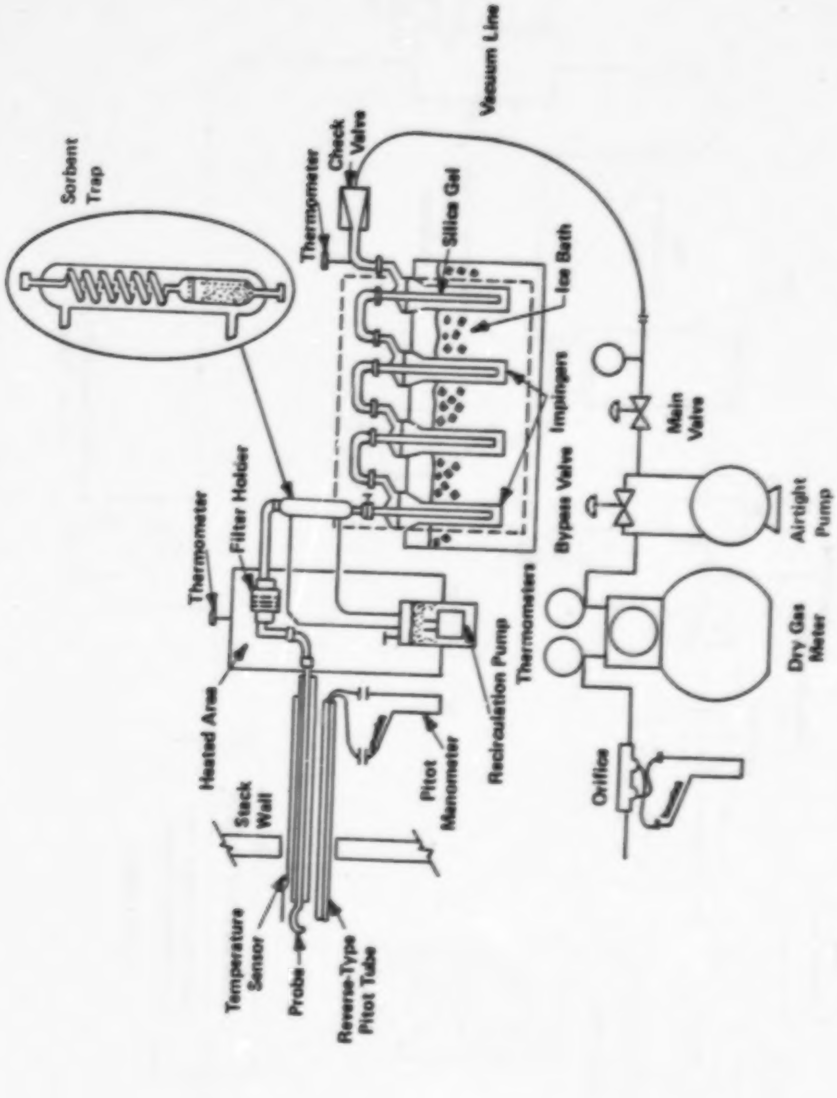
Sorbent Trap
Vacuum Line
Thermometer
Check Valve
Silica Gel
Ice Bath
Impingers
Thermometer
Filter Holder
Heated Area
Recirculation Pump
Stack Wall
Temperature Sensor
Probe
Reverse-Type Pitot Tube
Pitot Manometer
Thermometers
Bypass Valve
Main Valve
Airtight Pump
Dry Gas Meter
Orifice

Figure 2. Modified Method 5 train.

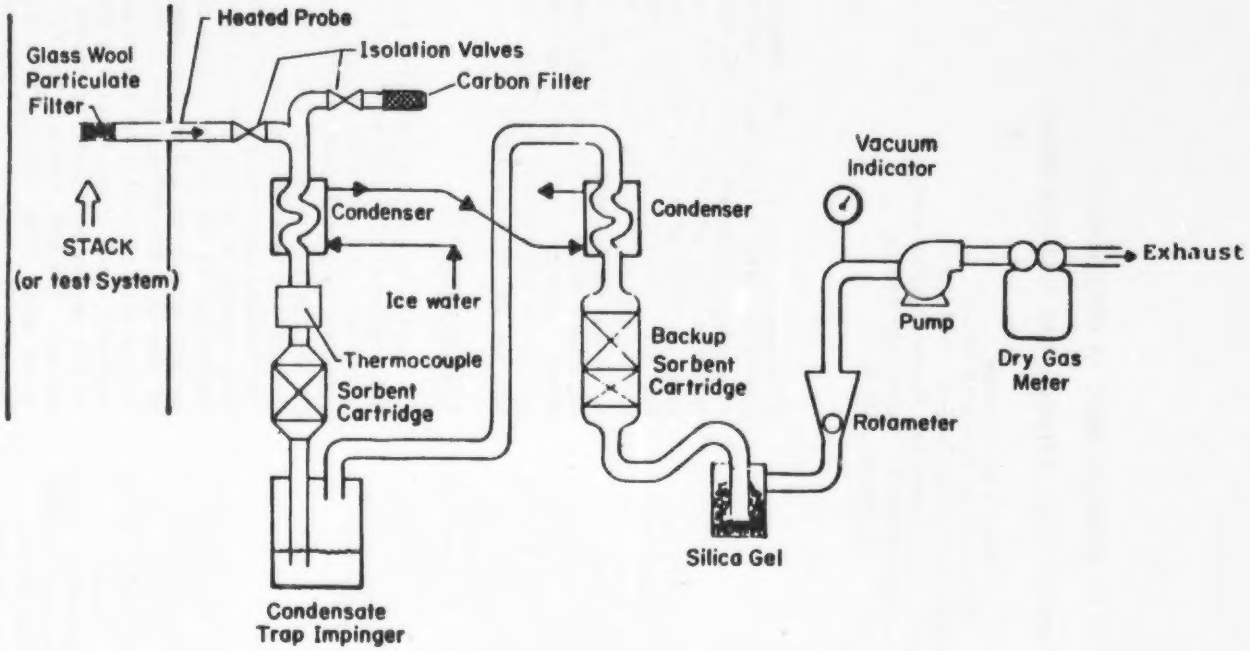
Heated Probe
Glass Wool Particulate Filter
Isolation Valves
Carbon Filter
STACK (or test System)
Condenser
Ice water
Condenser
Vacuum Indicator
Exhaust
Pump
Dry Gas Meter
Thermocouple
Sorbent Cartridge
Backup Sorbent Cartridge
Rotameter
Silica Gel
Condensate Trap Impinger

Figure 3. Volatile organic sampling train (VOST).

INCINERATION OF HAZARDOUS WASTE IN POWER BOILERS:

EMISSIONS PERFORMANCE STUDY RATIONALE AND TEST SITE MATRIX

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INTRODUCTION

Purpose

The purpose of this document is to summarize the background, rationale, and current study approach for the U.S. Environmental Protection Agency (EPA) research and assessment program relating to the incineration of hazardous waste in industrial boilers. The overall objective of the boiler program is to evaluate the technical and environmental acceptability of the use of hazardous wastes as fuels in industrial boilers, to aid in an Agency determination on the need for the nature of regulations of this practice under the Resource Conservation and Recovery Act (RCRA).

Background

Under RCRA, regulations and specific process performance standards have been developed and promulgated governing the issuance of permits for the operation of incinerator facilities for hazardous waste control (January 23, 1981). These standards, however, do not currently apply to the use of combustible hazardous wastes as fuels in energy recovery operations such as power boilers, process heaters, and high temperature industrial processes (cement kilns, steel furnaces, etc.).

The use of hazardous waste as fuels in power boilers is known to be a widespread practice. As much as 19 million metric tons of hazardous waste may be disposed of this way. EPA, however, has chosen to defer a regulatory decision on this practice because specific data on the extent of the practice were not available (i.e., number of sites, type of wastes, operating conditions), nor was there data on the destruction efficiency or the emissions performance of boilers employing hazardous waste as a fuel supplement. Other factors in this decision are documented in the Federal Register, Volume 45, No. 98, May 19, 1980.

Problem Definition

While an initial decision was made to not regulate hazardous waste incineration in boilers, it was also recognized that a potentially significant loophole existed in the regulatory structure. The same combustible hazardous waste which could be incinerated only under strict RCRA regulatory standards at the 300+ incineration facilities in the United States could also be incinerated as a fuel supplement in any of the over 400,000 boilers in the United States with virtually no environmental controls, save those involving the storage of the wastes and their transport to the boiler. The EPA, through the Office of Solid Waste (OSW) and the Office of Research and Development (ORD), initiated a program of research and performance testing to evaluate the engineering and environmental acceptability of hazardous waste incineration in boilers and to determine the need for and nature of regulatory standards to control the practice.

Because of the large number of facilities, boiler types and operating conditions, and wastes which potentially need to be evaluated with limited resources, a considerable amount of thought is necessary to carefully select a research and performance testing approach which optimizes the usefulness of the information collected.

The purpose of the balance of this document is to summarize the stepwise process, important assumptions, and rationale which form the basis for the boiler testing program now underway.

Limiting Assumptions

With limited funding available for field testing, any such test program must be directed toward obtaining only essential information in an economical manner. A test program that set out to attack the 450+ listed RCRA hazardous wastes across the full spectrum of boiler types in an unordered fashion would lack credibility and accomplish little in resolving the issue of whether boiler co-disposal of hazardous waste can be an acceptable practice. In 1975, there were about 400,000 industrial boilers of all sizes and types in operation. In order to be realistic, the test program must be directed toward boilers that are actually used to burn wastes, and combinations of wastes and boilers that truly represent test cases and will allow generalizing extrapolations to be made across the entire waste/boiler matrix.

Some simplifying assumptions can be made:

1. Each owner/operator of an industrial boiler will use his boiler only for disposal of in-plant generated wastes and will not likely accept waste from any other plant. The logic behind this assumption is that the primary advantage of boiler disposal (aside from energy conservation) is that the practice is exempt from RCRA regulations if the waste is not transported, stored, or disposed of off-site. Any facility which accepts wastes that are not produced onsite must be permitted as a Treatment, Storage and Disposal Facility (TSDF) under RCRA. To accept "imported" wastes could jeopardize the "exempt" status of the boiler facility.

2. Most hazardous wastes are generated by industry. This will exclude the large number of "industrial" size boilers that are located at commercial and institutional facilities such as shopping centers and hospitals.

3. It is unlikely that wastes will be burned in boilers smaller than 10 MM Btu/hr. This size (7,000 lb/hr of steam, 1.0 megawatts of electricity) is probably the minimum size at which combustion units can be retrofitted to accept significant quantities of wastes without negatively impacting the thermal operating characteristics of the units. Boilers below this size range are generally natural-gas or oil-fired firetube or cast iron units used for space heating. The 10 MM Btu/hr cutoff point is also convenient in the most boiler inventory reports (NEDS, EADS, etc.) do not report on boilers below that capacity. There are roughly 43,000 industrial boilers in the United States with capacities larger than 10 MM Btu/hr (1).

4. Most hazardous wastes that will be burned in boilers are generated by the organic chemicals industry. Table 1 describes the number of boilers with capacities larger than 10 MM Btu/hr for the top 10 hazardous waste generating SIC codes (2). As can be seen from Table 1, the largest hazardous waste generation is from the chemicals industry. The chemicals industry also has a large number of boilers. Therefore, the opportunity for disposal of hazardous wastes in boilers is greatest in the chemicals industry. The primary metal industries generate about 10 percent of the hazardous wastes, but wastes from this industry are less likely to be combustible than are wastes in the chemicals industry. The largest sources of organic hazardous wastes that are available to boilers for disposal are the chemicals, petroleum refining, and paper industries, in that order.

Through the application of these limiting assumptions, the universe of industrial boilers of concern can be reduced to less than 5,500. However, these 5,500 boilers are accessible to about 70 percent of total hazardous waste generation and over 95 percent of all potentially combustible hazardous wastes generated in the United States.

WASTE MATRIX DEVELOPMENT

Waste Property Consideration

Limiting consideration (for the purpose of scoping the proposed field testing program) to the three target industries greatly reduces the boiler population of concern. However, these three industries are known to generate over 400 of the 456 RCRA listed wastes in the F, K, P, and U Series. Of course, funding provisions do not allow for testing all 400 waste compounds against all 5,500 individual boilers. The wastes and boiler types must be ordered in such a manner that the limited test program answers the crucial question of which waste and boiler combinations are technically suitable and which are to be avoided.

As a first cut, wastes can be sorted into Good, Potential, and Poor candidates for combustion in any operation. This process was conducted in development of the Engineering Handbook for Hazardous Waste Incineration (3). The categorization process was approached as follows:

Waste Containing	Combustion Category
o Carbon, hydrogen, and/or oxygen	Good
o Carbon, hydrogen, ≤ 30 percent by weight, chlorine and/or oxygen	Good
o Carbon hydrogen, and/or oxygen, <30 percent by weight chlorine, phosphorous, sulfur, bromine, iodine, or nitrogen	Potential
o Unknown percent of chlorine	Potential
o Inorganic compounds	Poor
o Compounds containing metals	Poor

TABLE 1. BOILER POPULATION AND HAZARDOUS WASTE GENERATION BY SIC CODE (Reference 2)

	Hazardous Waste Generation		
	10^3 Metric TPY	% of Total	Number of Boilers w/Capacity $>10^7$ Btu/hr
28 Chemicals and Allied Products	25510	62.0	3346
33 Primary Metal Industries	4061	9.8	1417
29 Petroleum Refining	2118	5.1	1177
34 Fabricated Metals Products	1997	4.8	399
40 Non-Manufacturing Industries	1971	4.8	No Data
26 Paper and Allied Products	1296	3.1	1584
37 Transportation Equipment	1241	3.0	775
36 Electrical and Electronic Equipment	1092	2.6	318
31 Leather and Leather Products	474	1.1	No Data
35 Machinery	323	0.8	432

Of course, mixed wastes can contain compounds that represent each category. An appropriate testing matrix would encompass wastes from each category.

Incinerability

The wastes of concern can be sorted into good, potential, and poor candidates for incineration as a function of gross physical and/or chemical parameters as described above. However, once inorganic and metallic compounds are dismissed as incineration candidates, the remaining organic materials must be further categorized in some hierarchy of thermal stability to ensure that a variety of thermal, as well as physical conditions are examined. Each of the numerous approaches that have been taken to define "incinerability" to date can be best described as representing either one of two basic premises: kinetics or equilibrium. The kinetics premise assumes that the energy required to ignite a given molecule is the primary determinant of how difficult it is to "destroy" the molecule in combustion. The equilibrium premise holds that the energy required to complete the combustion process (to produce carbon dioxide and water) is the dominant concern. The kinetics approach is best represented by $T_{99.99}$. The equilibrium approach is best represented by the heat of combustion ΔHc/MW. For reasons presented in several forums, neither method is an unquestionably accurate description of "incinerability." However, EPA has chosen to utilize heat of combustion (in Kcal/gram) as the currently recommended Principal Organic Hazardous Constituents (POHC) selection criteria. The ΔHc approach will be the primary incinerability parameter used to select wastes for test firing in this boiler test program (4).

The main advantages of using the ΔHc method for boiler waste test firing are that the method is comprehensive (there exists at least a computed ΔHc for each waste in Appendix VIII) and that the waste/boiler selection can be fitted into the waste/incinerator permitting network. The ΔHc method is, as described earlier, an inexact incinerability measure. To subdivide the ΔHc listing too finely would be imputing more accuracy to the incinerability index than can be supported. Therefore, it is proposed here to divide the ΔHc list into three groups in describing difficulty to incinerate:

POHC Group	ΔHc Range (Kcal/g)
I	0 - 3.99
II	4.00 - 6.99
III	7.00 - 10.00+

This split results in three subgroups of roughly equal size. Examination of the POHC constituents within the categories lends some empirical credibility to the system. Materials in Group I tend to be highly halogenated ethylenes, benzenes, and ethanes. Group II contains lesser halogenated materials and process production bottoms. Group III contains the nonhalogenated solvents and solvent recovery bottoms. In essence, Group I contains materials that would not normally be considered for burning as fuels in the absence of RCRA. Group III contains materials that have historically been considered as candidate fuels for combustion operations.

Waste Classification Matrix

Three characteristics of a given waste material are important in mapping out a combustion testing program:

1. Thermal stability of the waste (incinerability)
2. Volume of waste generated in the United States
3. Physical state of the waste at 25°C.

The thermal stability of the waste is important in aiding waste selection that will provide information on the relative ease of destroying various waste types. The volume of waste produced is important in that a goal of the test program is to test realistic waste/boiler combinations. A low volume waste is less likely to be burned in a boiler than is a high volume waste. The physical state of the waste will impact the probability of boiler type selection. A waste that is a solid or a sludge will not likely be burned directly in a gas- or oil-fired boiler.

Table 2 provides an example matrix of waste POHC, waste identification code for some wastes that contain that POHC, waste description, annual waste production rate, and physical state of the waste at 25°C.

Table 3 summarizes the information in Table 2 in terms of EPA waste identification numbers. Implicit in this analysis is the assumption that wastes in mixtures retain their discrete properties.

TABLE 2. WASTE CLASSIFICATION MATRIX

		ΔHc (Kcal/g)	Representative Waste I.D.	Generation Rate MT/YR	State at 25°C
	POHC Group I:				
1.	Trichlorofluoromethane	0.11	F002	9,072	Liquid
2.	Tetrachloromethane (Carbon Tetrachloride)	0.24	K073	12,500	Liquid
3.	Hexachloroethane	0.46	K085	12,500	Solid
4.	Chloroform	0.75	K009	100,000	Liquid
5.	Tetrachloroethylene (Perchloroethylene)	1.19	F002	255,800	Liquid
6.	Methylene Chloride (Dichloromethane)	1.70	F002	213,000	Liquid
7.	Trichloroethylene	1.74	F002	181,000	Liquid
8.	Hexachlorobenzene	1.79	K030	40,000	Solid
9.	Trichloroethane	1.99	F002	181,000	Liquid
10.	Hexachlorobutadiene	2.12	K016	*	Solid
11.	Pentachlorophenol	2.19	K001	*	Solid
12.	Dichloroethane (Ethylene Dichloride)	3.00	K020	30,000	Liquid
13.	Trichlorobenzene	3.40	K015	1,800	Solid
14.	2,4 Dichlorophenol	3.81	K001	*	Solid
	POHC Group II:				
1.	Vinylidine Chloride	4.45	K020	*	Liquid
2.	Dichlorobenzene (1,2 Dichlorobenzene)	4.57	F002	11,800	Liquid
3.	Phthalic Anhydride	5.29	K022	*	Solid
4.	Nitrobenzene	5.50	K025	1,000	Liquid

Table 2 (continued)

	ΔHc (Kcal/g)	Representative Waste I.D.	Generation Rate MT/YR	State at 25° C
POHC Group II (cont.)				
5. Toluene Diisocyanate	5.92	K027	6,000	Solid
6. Chlorobenzene	6.60	F002	77,000	Liquid
POHC Group III:				
1. Acetonitrile	7.37	K014	6,000	Liquid
2. Phenol	7.78	K022	2,000	Solid
3. Pyridine	7.83	K026	*	
4. Acrylonitrile	7.93	K013	*	
5. Methyl Ethyl Ketone	8.07	F005	*	Liquid
6. Cresylic Acid	8.09	F004	*	Liquid
7. Cresols	8.18	F004	*	Liquid
8. Naphthalene	9.62	K060	*	Sludge
9. Benzene	10.03	K001	*	Solid
10. Toluene	10.14	K027	*	Liquid

* Undetermined Quantity

TABLE 3. WASTE MATRIX BY RCRA WASTE I.D. NUMBER

WASTE I.D.	POHC GROUP	PHYSICAL FORM	GENERATION RATE (MT/YR)
F001	I	Organic, Sludge, Solid	100,000*
F002	I, II	Liquid	100,000
F004	III	Liquid	-
F005	III	Liquid	-
K001	I, III	Solid	65,000
K009	I	Aqueous Liquid	-
K011	III	Aqueous Liquid	-
K013	III	Aqueous Liquid	6,000
K014	III	Organic Liquid	47,000
K015	I	Organic Liquid	50
K016	I	Organic Liquid	3,200
K018	I	Organic Liquid	35,000
K019	I	Organic Liquid	8,000
K020	I, II	Organic Liquid	125,000
K021	I	Aqueous Metallic Sludge	-
K022	II, III	Organic Sludge	100,000
K023	II	Liquid	-
K025	II	Organic Sludge	1,000
K026	III	Aqueous Liquid	1,000
K027	III	Organic Sludge	6,000
K029	I	Aqueous Liquid	1,200
K030	I, II	Organic Liquid	61,000
K036	III	Organic Sludge	-
K037	III	Aqueous Sludge	-
K042	III	Organic Solid	-
K073	I	Organic Liquid	125,000
K085	I	Organic Sludge	6,600
K095/96	I	Organic Liquid	34,000

* Estimated 10 percent of Production.
- Undetermined Quantity

Aside from thermal stability, selected waste characteristics may be desirable from a testing perspective. Two characteristics that may be complicating factors from a combustion perspective are the presence of significant amounts of water and metal contaminants in the wastes. A hierarchy of wastes in descending order of difficulty to destroy in boilers can be envisioned as follows in Table 4:

TABLE 4. WASTE CLASSIFICATION MATRIX

	CHARACTERISTICS	WASTE TYPE EXAMPLE(s)
	Group I, Aqueous	K001, K009, K029
	Group I, Metals	K021
↑ WORST CASE	Group I, Nonaqueous	F001, F002, K015, K016, K018, K073, K085
	Group II	F002, K020, K022, K023, K025, K036
	Group III, Aqueous	K011, K013, K026, K037
	Group III, Metals	
	Group III, Nonaqueous	F003, F004, F005, K001, K014, K022, K027, K036, K042

BOILER MATRIX DEVELOPMENT

Boilers in the Chemical Industry

The purpose of this testing program is to demonstrate to what degree and which boilers are capable of destroying which waste. Since the focus of the study has been determined to be the chemicals industry, we are interested in testing boilers that are actually used in that industry.

Table 5 describes the types and capacities of boilers used in the chemicals industry. By far the largest number of boilers are oil (46.2 percent) or gas (42.0 percent) fired units. Coal (10.3 percent) and waste (1.5 percent) fired boilers are far less represented in the chemicals industry. Coal boilers do make up 13.8 percent of total boiler capacity, indicating that the average coal boiler is larger than either the average gas- or oil-fired unit.

TABLE 5. BOILERS IN THE CHEMICALS INDUSTRY (SIC 28) (Reference 2)

FUEL TYPE	NUMBER OF BOILERS IN SIZE RANGE (10^6 Btu)						TOTAL NO. BOILERS	TOTAL CAPACITY (10^9 Btu)	% TOTAL CAPACITY
	10-50	50-100	100-200	200-400	400-700	700-1250			
Gas	542	276	261	206	109	11	1405	196.78	45.6
Oil	679	351	299	150	61	8	1548	168.12	38.9
Waste	13	13	12	10	1	1	50	7.25	1.7
Coal	41	74	128	77	21	2	343	59.55	13.8
TOTALS	1,275	714	700	443	192	22	3346	431.70	100.0

Existing Data and Previous Studies

Substantial data exists on emissions of regulated criteria pollutants from power boilers. However, there exists no data base on destruction of hazardous chemical compounds in industrial boilers. Source emissions data for regulated pollutants may be useful in characterizing a given boiler's ability to destroy hazardous chemical compounds. These will be discussed in more detail in a subsequent section of this document. Some attempts have been made to directly assess the capabilities for boiler destruction of hazardous wastes through modelling and engineering analysis. These attempts will be discussed in this section.

In two separate studies, conducted in 1980 and 1981, Acurex Corporation examined thermal conditions for distinct boiler types (1, 5). Time above temperature predictive plots were developed for each boiler type. Fuel particle path analyses were conducted at full and half loads. The environment that each boiler presented to a given fuel was described in terms of conditions of time and temperature required for heating, volatilization, thermal cracking, and oxidation of the fuel. Zonal heat balances were applied to estimate conditions at each point in the boiler.

The Acurex analysis produced some general conclusions. It appeared that the larger the boiler the greater the likelihood that conditions for waste destruction will exist. The medium-sized watertube units present mean conditions that are conducive to destruction of most wastes but have significant potential for excursion into conditions not favorable for waste destruction at the margins of operating conditions. The firetube boilers present high temperatures and good flame exposure but the fuel residence time appears to be of insufficient duration to allow for volatilization and oxidation of the waste fuel particles.

Waste Destruction Surrogates

In the absence of specific waste Destruction and Removal Efficiency (DRE) data for boiler firing of hazardous wastes, examination of some boiler operational parameters and stack emissions data could prove helpful in assessing a boiler's ability to destroy hazardous wastes. None of these candidate DRE "surrogates" have been verified in experimentation or testing but discussion of the various available parameters is of some value.

DRE is primarily a function of temperature. Flame exposure, residence time, and mixing are also factors that affect the degree of oxidation of a particular molecule. For a boiler with all other factors held constant, waste destruction will more than likely occur as described below:

DRE will increase as the following items increase:

Boiler load
Mean gas temperature
Mean gas residence time
CO_2 emissions
NO_x emissions

DRE will increase as the following items decrease:

Excess air
O_2 emissions
Boiler surface-to-volume ratio
CO emissions
Total HC emissions

Examination of the above listing leads to a winnowing out process. While it is true that boiler combustion efficiency increases with load up to optimum (generally nameplate) output conditions, it is also true that the same boiler can operate at different load conditions. Boiler load is not a machine characteristic but an operating characteristic and cannot be used to distinguish between boiler types. The same statement can be made concerning excess air, CO_2 emissions, and O_2 emissions. Excess air is largely a function of load conditions. CO_2 and O_2 emissions are excess air- and load-dependent.

Table 6 describes pertinent machine specific parameters and emissions that can be used to classify boilers with respect to their estimated ability to destroy hazardous compounds (1, 6, 7, 8). Each of the parameters presented in Table 6 will be described in detail.

Mean gas temperature and residence times are significant from a waste kinetics perspective and were utilized extensively in the Acurex analysis. However, at temperatures above the kinetics operating zone and in the presence of a flame, time-temperature paths are not sufficient to fully describe compound destruction and require detailed knowledge of the kinetic behavior of the target compounds to be effective.

Table 6 does show that while the temperatures in the firetube boilers are very high, the bulk gas residence times are so short that there is less certainty that all particles of a given material will "experience" the complete kinetics process (e.g., volatilization, pyrolysis, ignition).

TABLE 6. BOILER CLASSIFICATION PARAMETERS (References 1, 6, 7, 8)

BOILER TYPE	BOILER FUEL	BOILER SIZE (MM Btu/hr)	EXIT T (°F)	RESIDENCE t (sec)	S/V RATIO	CO ng/J	HC ng/J	NO_x ng/J
Firetube	Natural Gas	10-50	2400	0.23	1.60	8	3.4	42
Firetube	Oil	10-50	2400	0.22	1.60	15	1.7	59
Watertube	Natural Gas	10-100	2300	0.50	0.80	15	2.4	156
Watertube	Oil	10-100	2300	0.50	0.80	14	3.7	156
Watertube	Stoker Coal	10-100	2060	1.50	0.30	146	3.6	155
Watertube	Stoker Coal	100+	2000	1.90	0.22	86	1.7	240
Watertube	Natural Gas	100+	2200	0.82	0.52	17	0.7	232
Watertube	Oil	100+	2000	0.77	0.52	14	3.0	190
Watertube	Pulverized Coal	150+	2000	1.82	0.27	10	1.7	361

Surface-to-volume ratio (S/V) is important as a descriptor for a potential DRE failure mechanism -- gas quenching. The larger the boiler tube surface with respect to the total furnace volume, the more likely that a particle of waste material will experience something less than mean furnace temperature. As expected, S/V generally decreases with boiler size. The principal exception to this rule is the case of coal fired boilers. For coal boilers, the fuel temperature must be kept below the ash fusion temperature to avoid slagging and fouling. This lower temperature operation requires that, in order to produce a given pound of steam, a given coal boiler must be much larger than an equivalent oil- or gas-fired boiler. Therefore, furnace heat liberation rates for coal-fired boilers are much lower than for other types of boilers (by a factor of from 2 to 10). This factor largely explains why coal boilers tend to be much larger (capacity and size-wise) than other boilers. The net effect is that while larger boilers have lower S/V ratios than smaller boilers, coal boilers have even lower S/V ratios than either oil or gas boilers in a similar size range.

CO and HC emissions may be machine specific and are a measure of the completeness of combustion. Unfortunately, these emissions are also fuel- and operational-dependent. Two coals or oils may produce different CO and HC emissions due to different fuel and operational conditions. Two different machines burning the same fuel under "optimum" operating conditions may yield meaningful CO and HC data. In a similar manner, HC and CO emissions from the same boiler may provide useful surrogate data on compound destruction. However, the AP-42 data presented in Table 6 is compiled in an a posteriori manner and is not useful in characterizing DRE.

Data on NOx emissions, on the other hand, can be very useful in describing a given boiler's potential to destroy waste. The importance of NO_x emissions as a boiler classification tool is discussed in the next section.

Nitrogen as a POHC Surrogate

Production of oxides of nitrogen (NO_x) from fuelborne nitrogen occurs relatively easily in combustion operations. However, production of NO_x from airborne nitrogen is an extremely energy intensive operation that occurs ony at elevated temperature (assuming atmospheric pressure). In the temperature regions in which boilers operate far more NO_x is produced from air than from fuel. Therefore, in a boiler, the most likely process for production of NO_x is the cracking of the N_2 molecule to N^+ and the oxidation of the N^+ to form NO_2, No_3, etc.
This highly energy intensive process is thermodynamically similar to that required to break a carbon = carbon double bond or a carbon - chlorine bond and produce CO and CO_2 from fuel. Therefore, all other things being equal, the tendency of a given boiler to produce NO_x should be a rough measure of that boiler's ability to destroy a waste compound. Of course, all things are never equal but this sort of macroapproach is well suited toward use of the AP-42 data presented in Table 6.

Rearranging the presentation of the data in Table 6 so that boilers are displayed in terms of ascending NO_x emissions and deleting the CO and HC daa, we obtain Table 7. Examination of Table 7 yields boilers ranked in ascending order of size (capacity). Also, it should be noted that within boiler fuel types, the ranking by size is rigidly adhered to (i.e., the smallest oil boiler listed has the lowest characteristic NO_x emissions of all oil boilers; likewise, the largest oil boiler has the highest characteristic NO_x emissions). Similar boiler types (e.g., firetubes) have similar NO_x emissions.

TABLE 7. BOILERS RANKED IN TERMS OF HISTORICAL NO_x EMISSIONS

BOILER TYPE	BOILER FUEL	BOILER SIZE (MM Btu/hr)	NO_x Ng/J	S/V RATIO	EXIT T (°F)	RESIDENCE (sec)
Firetube	Natural Gas	10-50	42	1.60	2400	0.22
Firetube	Oil	10-50	59	1.60	2400	0.23
Watertube	Stoker Coal	10-100	155	0.30	2060	1.50
Watertube	Natural Gas	10-100	156	0.80	2300	0.50
Watertube	Oil	10-100	156	0.80	2300	0.50
Watertube	Oil	100+	190	0.52	2000	0.77
Watertube	Natural Gas	100+	232	0.52	2200	0.82
Watertube	Stoker Coal	100+	240	0.22	2060	1.90
Watertube	Pulverized Coal	150+	361	0.27	2060	1.82

Boiler Classification Matrix

Through utilization of Tables 5, 6 and 7, a boiler matrix can be developed. The size and type breakdown in Table 7 conforms to AP-42 structure and need not impose a constraint on matrix development but should be used as a guide to boiler selection. However, function as well as convenience is served by generally adhering to these categories.

From Table 7, firetube boilers represent a suspected worst case for waste destruction. From Table 5, over one-third of the boilers found in the chemicals industry are in the size range of 10 to 50 MM Btu/hr. Not all of those small boilers are firetubes, but all firetube boilers are found in this size range. From Table 7, regardless of fuel type, the firetube boilers perform and appear to be identical. Therefore, one boiler matrix constituent will be "Firetube Boilers."

The oil- and gas-fired watertube boilers in the 10 to 100 MM Btu/hr size range are twins and should be grouped together (Table 7). The size range spread may appear to be large. However, such a cut makes sense when we consider that, at about 100 MM Btu/hr, boiler design practice is to go from single or multiple burner configurations. The larger and more uniform flame zone should provide for more constant and harsher combustion conditions with the boiler.

The oil- and gas-fired boilers in the greater than 100 MM Btu/hr size range should also be grouped together. From Table 5, those boilers account for approximately 30 percent of the population of boilers in the chemicals industry. Too fine a breakdown would be of little merit, particularly since this size range appears to be biased toward a best case with increasing boiler size.

Coal boilers warrant little attention due to their small presence in the chemicals industry (Table 5). However, coal boilers have two characteristics which mandate interest: 1) the ability to accommodate waste solids and sludges and 2) low S/V ratios, long residence times and relatively high NO_x emissions. The ability to handle solids is unique to coal boilers. The latter point makes coal boilers a potential best case. Examination of Table 5 yields that the critical mass of coal boilers in the chemicals industry is in the larger size range (100 to 400 MM Btu/hr), little difference between pulverized coal and stoker boilers with respect to physical and operating characteristics. The higher NO_x emissions for the pulverized coal boilers would be a function of size rather than type of boiler. A single coal-fired boiler entry on the matrix will be sufficient.

Table 8 lists the boiler categories on the test matrix in ascending order of assumed ability to destroy wastes.

WASTE/BOILER TEST MATRIX

Waste/Boiler Matrix Format

By overlaying the boiler test matrix from Table 8 onto the waste classification matrix from Table 4, one can obtain a waste/boiler test matrix format. This format is described in Table 9.

TABLE 8. BOILERS RANKED IN ASCENDING ORDER OF ASSUMED ABILITY TO DESTROY WASTES

	CASE I.D.	BOILER TYPE	FUEL TYPE	CAPACITY RANGE (MM Btu/hr)
	A	Firetube	Oil, Gas	10-50
WORST CASE ↑	B	Watertube	Oil, Gas	10-100
	C	Watertube	Oil, Gas	100+
	D	Watertube	Coal	100+

TABLE 9. ECONOMY WASTE/BOILER TEST PROGRAM
(12 Tests)

				WORST CASE BOILER DESCRIPTIONS			
	WASTE DESCRIPTORS		CASE I.D.	A	B	C	D
			BOILER TYPE	FIRETUBE	WATERTUBE	WATERTUBE	WATERTUBE
			FUEL TYPE	OIL, GAS	OIL, GAS	OIL, GAS	COAL
	POHC GROUP	PHYSICAL QUALIFIERS	CAPACITY (106 Btu/hr)	10-50	10-100	100+	100+
	I	AQUEOUS		X	X		
		METALS					
		SOLIDS		N/A	N/A	N/A	X
		NON-AQUEOUS		X	X	X	
WORST CASE	II				X		
		AQUEOUS			X		
	III	METALS					
		SOLIDS		N/A	N/A	N/A	X
		NON-AQUEOUS		X	X	X	

NA - Not Applicable

Utilizing Table 9, we can structure a test program that comprehensively covers the spectrum of waste and boiler types or one that encompasses only boundary conditions within a proscribed budget.

The wastes are described by POHC Group and Physical Qualifiers that may impact boiler type selection and waste destruction. "Aqueous" implies significant water in the waste. "Metals" refers to the presence of inorganic or metallic contaminants in the waste which could present problems for the boiler. "Solids" refers to the waste containing solid materials or sludges. "Non-aqueous" refers to a waste with no significant water, solids, or contaminants. Of course, a given waste could contain a combination of conditions. All permutations are not shown but can be accommodated within the matrix. It may be argued that a highly aqueous Group III waste can be a worse case than a non-aqueous Group I waste. The wastes are arrayed from top to bottom in order of assumed worst to assumed best case. Group II wastes are not broken down further since these are not assumed to be limiting conditions.

The boilers are described by firebox type, fuel type, and capacity. The boilers are arrayed from left to right in order of assumed worst to assumed best case. Certain physically constraining cases can be assumed to exist. For example, it is unlikely that a solid-containing waste can be burned in an oil- or gas-fired boiler unless that boiler has been converted to a liquid fuel from a coal operation or the waste fuel has been volatilized in some preprocessing application.

Additionally, air pollution control devices (APCDs) are not factored into the matrix. Smaller industrial boilers (10 to 50 MM Btu) generally have no APCDs. Larger coal-fired boilers may have multiclones (stokers) or electrostatic precipitators (pulverized coal), but large oil- and gas-fired industrial boilers generally have no APCDs. It is felt that the addition of factors for presence, absence, or types of APCD would overly complicate the matrix discussion.

Test Program Selection

Ideally, of course, a comprehensive test program would involve at least one test of each waste/boiler combination and permutations of each combination described in Table 9. Such a test matrix would require completion of at least 60 tests.

However, EPA currently has sufficient funds for only an "economy" 12-test program. Such a truncated program must focus on "worst case" conditions. Limited testing would be conducted on "best case" wastes and only one Group II verification test could be tested. Comprehensive testing of the most representative boiler type (B) would be emphasized. Little exploration of qualifying waste conditions (metals, aqueous) would be conducted. Hopefully, this program, supported by pilot-scale parametric testing, would provide an "envelope" around acceptable waste/boiler combinations.

Utility and Flexibility of the Matrix

Almost every conceivable waste and standard boiler combination will fit into the waste/boiler matrix. Ideally, access to all types of wastes and boilers can be secured. In the "real" world of testing targets of opportunity, the matrix can serve as a guide to test selection. For instance, if eight test candidates are available, the matrix would help ensure that five III B tests are not selected.

Waste volume is also a concern. For example, if there exists a choice between two IB combinations, the waste that has the highest national generation rate would be selected.

Cautions On the Use of the Matrix

The matrix is a tool for ordering a testing program. Implicit in its use are certain assumptions. The first assumption is that all boilers are operated equally expertly. It is conceivable that all boilers, if well designed and perfectly operated, can achieve DREs of 99.99 percent. Within boiler types the overriding factor concerning waste destruction is boiler operation. It is entirely probable that a well operated "worst case" boiler will outperform a poorly operated "best case" boiler.

The second assumption is that addition of the waste material to the boiler does not alter boiler operating characteristics. Any waste added in abundant quantities will indeed have an effect on boiler operating conditions.

The third assumption is that all wastes are equally likely to be burned in all boilers. In fact, due to their potentially damaging impact on boiler hardware, certain wastes (particularly Group I highly chlorinated materials) may not be burned in boilers at all.

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OBSERVATIONS OF FLUID DYNAMIC EFFECTS UPON HIGH-TEMPERATURE DESTRUCTION OF ORGANIC COMPOUNDS

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ABSTRACT

In the controlled high-temperature incineration of industrial organic wastes, events that occur in the gas-phase are of vital importance. Within a rotary kiln-afterburner incinerator the large volume afterburner chamber is responsible for the complete destruction of organic materials that survive, or are emanated from the previous exposures.

The fluid dynamic behavior of the high-temperature gas phase has been examined with special attention to the various aspects of exposure time and fluid interaction of gas-phase substances. These observations with respect to destruction efficiency of organic substances have been made on the laboratory-scale, and several implications can be drawn with respect to the gas-phase decompositions of both hazardous organic compounds and their thermal reaction products.

RESEARCH PROJECTS AT EPA'S LOUISIANA STATE UNIVERSITY HAZARDOUS WASTE RESEARCH CENTER - USEPA CENTER OF EXCELLENCE

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ABSTRACT

Now beginning its third year of operation, the Hazardous Waste Research Center at Louisiana State University is conducting fundamental and exploratory research in three general areas: chemical/material interactions, incineration, and alternate methods of treatment/destruction. The research projects range from studies on the rates of supercritical extraction of organics from solids to the destructibility of pure chlorinated hydrocarbons in laboratory flames to an investigation of bonding mechanisms associated with cement - stabilized organics. Although administered through LSU's College of Engineering, individual research projects are being conducted by multidisciplinary groups representing a number of academic departments.

In addition to its fundamental and exploratory research efforts, the Center has active and expanding programs in the areas of applied research and technology transfer. The applied research component will encompass projects of more immediate interest to federal and state agencies and to private industry. The objective of the technology transfer activities is to disseminate state-of-the-art technology and research advances to the professionals in government and industry and also to the nonprofessional public. These latter efforts are beyond the scope of the EPA-funded exploratory research center and are supported by the university, other governmental agencies, and private industry.

HAZARDOUS WASTE CONTROL TECHNOLOGY DATA BASE

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ABSTRACT

The Hazardous Waste Control Technology Data Base (HWCTDB) is an automated data base sponsored by EPA's Incineration Research Branch to store detailed technical data relevant to the thermal destruction of hazardous wastes. The data base stores design, operating, and performance data obtained from incineration facility permit applications, trial burn reports, research and development projects, and literature sources. The data base went on-line in late 1982.

EVALUATION OF AN ADVANCED LOW NO_x HEAVY OIL BURNER FOR INCINERATION OF NITRATED HAZARDOUS COMPOUNDS

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ABSTRACT

Among the RCRA-listed hazardous waste compounds is a variety of chemical species which are highly nitrated. During the combustion of these compounds the bound nitrogen atom is readily oxidized to form nitrogen oxide (NO) in the incinerator or boiler exhaust. Limited test data has shown that co-firing nitrobenzene with natural gas in an industrial boiler increased NO_x emission by a factor of 6 to 9 when the nitrobenzene feed rate represented only 6 percent of the input heating value. Accordingly, a concern exists that classical incineration of such materials may exchange destruction of the waste for a potential NO_x emission problem.

A significant body of data on the pyrolysis of nitrated compounds is available from the EPA NO_x control program. Species such as nitrobenzene, acrylonitrile, and aniline were previously studied as possible model compounds for nitrogen bound within the structure of coal and heavy residual fuel oils. Those pyrolysis studies clearly indicated that hydrogen cyanide was the dominant nitrogen species evolved. Accordingly, incineration of this class of waste raises concern that HCN would be a potential product of incomplete combustion (PIC) and that emission of that PIC would be of equal or greater concern than emission of the principal organic hazardous compound (POHC).

Based upon considerations such as those identified above, a need exists for combustion technology which could assure high destruction efficiency for the POHC and probable PIC and simultaneously minimize the emission of NO_x. To accomplish that objective requires a combustor which establishes an extremely high temperature, fuel-rich primary combustion zone followed by an excess air burnout region. A fuel-rich primary zone would shift nitrogen equilibrium almost totally to N_2 whereas fuel-lean equilibrium is substantially shifted toward NO formation. The high temperature promotes initial destruction of the POHC but also accelerates chemical kinetic processes driving fixed nitrogen species (such as any HCN PIC) to N_2.

As part of the EPA NO_x control program, combustion techniques such as that described above have been previously established. A three million Btu/hr version of this burner is available at the in-house research facilities of IERL/RTP and a 60×10^6 Btu/hr version is currently being field tested in Kern County, California, on an enhanced oil recovery steam generator. The current paper reports on an evaluation of this low NO_x burner technology for incineration of three highly nitrated hazardous compounds. Test results are presented on the destruction efficiency of the POHC, emission of HCN and NO_x while burning nitrobenzene, aniline, and acrylonitrile. All waste compounds were doped into distillate fuel oil at concentrations of 5 and 25 percent by weight. Test results are being evaluated prior to proceeding with a full-scale field verification of this technology.

REGULATORY SUPPORT RESEARCH STUDIES SUPPORTED BY EPA/CINCINNATI MSD COOPERATIVE AGREEMENT

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ABSTRACT

A number of research studies have been proposed and carried out to produce information on various aspects of a publicly owned, full scale hazardous waste incinerator. These studies are intended to produce data to assist in the development, support and revision of EPA's regulatory responsibilities addressing hazardous waste incinerators. Typical studies that have been carried out include: the preparation of a design and economic history of the incinerator complex, evaluation of options for acid neutralization in combustion gases, evaluation of DRE capabilities and potential monitors, and testing of alternative modifications to particulate emission control devices. Anticipated studies include: developing a detailed understanding of ash characteristics with regard to hazardous properties, testing of various pilot scale particulate control devices, and preliminary evaluation of a colorimetric DRE monitor.

FLAME-MODE HAZARDOUS WASTE DESTRUCTION RESEARCH

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ABSTRACT

The results of a laboratory-scale study of flame-mode hazardous waste incineration are reported. The primary goal of the work was to compare the various incinerability ranking procedures with rankings generated under flame conditions typical of liquid-injection incinerators. A secondary objective was the comparison of flame and non-flame thermal destruction behavior. We previously reported (Ninth SHRD Symposium) that, when operated under efficient combustion conditions, flames nearly quantitatively destroy organic waste compounds. For incomplete destruction to take place, the flame must be perturbed into inefficient operation. The compound rankings resulting from these perturbed states (termed failure conditions) were dependent on the cause of the perturbation. The results presented here represent an extension of the previous work.

The results were generated using a 65 Kilowatt (kW) turbulent liquid spray flame. The flame enclosure was cooled to concentrate on flame-zone processes by quenching post-flame reactions. In the present study the flame was fired on No. 2 fuel oil doped with four model waste compounds (3% by weight): Benzene, chlorobenzene, chloroform and acrylonitrile. The flame was operated under high efficiency conditions by high and low excess air, by degraded fuel spray atomization quality, and by impingement of the flame on a cold surface. The destruction efficiency was measured by Tenax trapping of the stack effluent followed by thermal desorption and gas chromatographic/flame ionization detector analysis. Simultaneous measurements of CO, CO_2, O_2, CH_4 and total unburned hydrocarbons were obtained.

The results sustained the previously reported conclusions that flames are capable of high DE, and that loss of this high DE is necessarily due to perturbation of the flame into a failure condition. Waste DE rankings were found to be dependent of flame condition. The new results also indicated that a linear relationship exists between DE and unburned hydrocarbon emissions from the flame zone. Correlation of DE and CO measurements showed that CO emissions must increase to substantial levels before DE begins to degrade. It should be emphasized that these flame-zone results may be modified by realistic post-flame time-temperature histories.

These results suggest a performance monitoring and control methodology in which the difference between a correctly operating incinerator and a failure mode can be detected. The CO measurement could be used as an early indication of the approach of a failure condition. It could also be used as a means of controlling operating parameters. Total hydrocarbon measurement could be used to indicate the presence of a failure condition. Significant hydrocarbon emissions could be used to shut down waste flow.

EVALUATION AND DEVELOPMENT OF INNOVATIVE INCINERATION TESTING PROCEDURES

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ABSTRACT

This study investigated innovative real-time monitoring techniques for hazardous waste incineration. The objectives were to survey and select monitoring systems that measured (either directly or indirectly) destruction and removal efficiency (DRE), and to demonstrate the effectiveness of the selected system in a test program. Seven potential monitoring systems were evaluated using the criteria of operating characteristics, limitations, applications, degree of development, and cost. The selected system was an in-line flame ionization detector (FID) that measures total organic carbon in the stack.

Tests were performed at the EPA's Combustion Research Facility in Pine Bluff, Arkansas. Six test runs were conducted using hexachlorobenzene and/or toluene as surrogate hazardous wastes. Total organic carbon concentrations corresponded in the same direction and magnitude as the DRE values as measured by Method 5 stack tests. The results from these tests indicate that the selected approach is a promising system for on-line, real-time monitoring of incinerator performance.

From the results of these tests it is recommended that further study be performed to quantify the relationship between TOC concentration and POHC destruction and removal. Appropriate relationships need to be rigorously challenged and tested if TOC concentration is to become an accepted method for monitoring DRE values.

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